Synthesis and Physicochemical Characterization of Heavily Doped CuInS2 Diamond-Like Semiconductors

Johanna D. Burnett

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SYNTHESIS AND PHYSICOCHEMICAL CHARACTERIZATION OF HEAVILY DOPED CuInS$_2$ DIAMOND-LIKE SEMICONDUCTORS

A Dissertation
Submitted to the Bayer School of Natural Sciences

Duquesne University

In partial fulfillment of the requirements for the degree of Doctor of Philosophy

By
Johanna D. Burnett

December 2013
ABSTRACT

SYNTHESIS AND PHYSICOCHEMICAL CHARACTERIZATION OF HEAVILY DOPED CuInS$_2$ DIAMOND-LIKE SEMICONDUCTORS

By

Johanna D. Burnett

December 2013

Dissertation supervised by Dr. Jennifer A. Aitken.

Cu$_{1-x}$Fe$_x$S$_2$ ($x = 0 - 0.30$), Cu$_{1-x}$Li$_x$InS$_2$ ($x = 0 - 0.40$), and Cu$_{1-x}$Li$_x$In$_{0.90}$Fe$_{0.10}$S$_2$ ($x = 0 - 0.40$) were synthesized via high-temperature, solid-state synthesis. Rietveld refinements of the neutron and synchrotron powder diffraction data of Cu$_{1-x}$Fe$_x$S$_2$ ($x = 0 - 0.15$) indicate that all Fe-substituted materials are phase pure with the exception of the CuIn$_{0.85}$Fe$_{0.15}$S$_2$ sample, which contains a minute secondary phase. These refinements also verify that iron resides on the indium site in the CuIn$_{1-x}$Fe$_x$S$_2$ materials. Inductively coupled plasma (ICP) confirms that the actual stoichiometry is close to the nominal composition of the materials. Analysis of X-ray photoelectron spectroscopy (XPS) spectra determined the oxidation state of the copper, indium, and sulfur ions (Cu$^{1+}$, In$^{3+}$, and S$^{2-}$), and Fe$^{57}$ Mössbauer spectroscopy verified that the iron is in the 3+ oxidation state.
CuIn$_{0.875}$Fe$_{0.125}$S$_2$ displayed the lowest total thermal conductivity of the Fe-substituted CuIn$_2$ series, 1.37Wm$^{-1}$K$^{-1}$ at 570K, as well as the highest thermopower, -172$\mu$VK$^{-1}$ at 560K. The electrical conductivity increases over six times upon going from CuInS$_2$ to CuIn$_{0.875}$Fe$_{0.125}$S$_2$. These improved properties result in an increase in the ZT of CuInS$_2$ by over an order of magnitude for the x = 0.125 sample. Magnetic measurements reveal the x = 0 - 0.10 samples to be paramagnetic, while the sample in which x = 0.125 displays ferromagnetic ordering below 95K. A band gap of the CuIn$_{1-x}$Fe$_x$S$_2$ solid solution was estimated to be in the range of 0.70 – 1.07eV, while Li-substitution increased the band gaps of the Cu$_{1-x}$Li$_x$In$_2$ series by a maximum of 0.31eV and the Cu$_{1-x}$Li$_x$In$_{0.90}$Fe$_{0.10}$S$_2$ series by a maximum of 0.33eV.
DEDICATION

This work is dedicated to Emma Ashley Burnett, who continues to inspire, motivate, and awe me each day.
I could never have accomplished this work were it not for the strength and grace of God. The full support of my family has allowed me to pursue my passion for research and education. I would like to particularly thank my husband, Joel Burnett, for not only his love and patience, but also for his tireless availability as tech support, chef, chauffeur, secretary, and nurse. Many thanks to Emma Burnett for studying and working with me, as well as serving as a faithful sounding board for my many presentation practice sessions. I would also like to acknowledge Patricia Reilly, Rebecca and David Quel, Marilyn Lucas, Allen Burnett, Sarah Burnett, and Joshua and Georgia Burnett for your encouragement, patience, and understanding of missed Birthdays and other such familial atrocities. The memories of, and the lessons learned from my grandmothers Laverne Anderson and Della Reilly, who have passed on, have helped to provide me with strength and perseverance.

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TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abstract</td>
<td>iv</td>
</tr>
<tr>
<td>Dedication</td>
<td>vi</td>
</tr>
<tr>
<td>Acknowledgement</td>
<td>vii</td>
</tr>
<tr>
<td>List of Tables</td>
<td>xiv</td>
</tr>
<tr>
<td>List of Figures</td>
<td>xvii</td>
</tr>
</tbody>
</table>

Contents

1. An Introduction to Diamond-Like Semiconductors..............................................1
   1.1 Introduction.................................................................................................1
   1.2 Fundamentals of Diamond-Like Semiconductors...........................................2
   1.3 Introduction to Photovoltaics........................................................................4
       1.31 Photovoltaic Cells....................................................................................5
       1.32 Diamond-Like Semiconductors of Current Interest for Photovoltaic Applications....................................................................................6
       1.33 Targeting New DLSs with Photovoltaic Applications...............................7
   1.4 Introduction to Thermoelectrics (TEs).......................................................8
       1.41 Thermoelectric Devices...........................................................................9
       1.42 Targeting New DLSs With Thermoelectric Applications..........................12
   1.5 Magnetic Properties.......................................................................................13
   1.6 References.....................................................................................................15
2. Materials Characterization

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1 Introduction to Materials Characterization</td>
<td>20</td>
</tr>
<tr>
<td>2.2 X-Ray Photoelectron Spectroscopy</td>
<td>21</td>
</tr>
<tr>
<td>2.3 $^{57}$Fe Mössbauer Spectroscopy</td>
<td>27</td>
</tr>
<tr>
<td>2.4 Time of Flight Neutron Powder Diffraction</td>
<td>30</td>
</tr>
<tr>
<td>2.5 Thermoelectric Measurements</td>
<td>35</td>
</tr>
<tr>
<td>2.5.1 Sample Densification and Determination of Sample Density</td>
<td>35</td>
</tr>
<tr>
<td>2.5.2 Thermal Conductivity</td>
<td>37</td>
</tr>
<tr>
<td>2.5.3 Thermopower and Electrical Conductivity</td>
<td>38</td>
</tr>
<tr>
<td>2.6 References</td>
<td>41</td>
</tr>
</tbody>
</table>

3. Location and Oxidation State of Iron in Fe-substituted CuInS$_2$ Chalcopyrites

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1 Introduction</td>
<td>43</td>
</tr>
<tr>
<td>3.2 Experimental</td>
<td>46</td>
</tr>
<tr>
<td>3.2.1 Reagents and Synthesis</td>
<td>46</td>
</tr>
<tr>
<td>3.3 Physical Measurements</td>
<td>47</td>
</tr>
<tr>
<td>3.3.1 X-ray Powder Diffraction (XRPD) and Rietveld Refinement</td>
<td>47</td>
</tr>
<tr>
<td>3.3.2 Optical Diffuse Reflectance UV/VIS/NIR Spectroscopy</td>
<td>48</td>
</tr>
<tr>
<td>3.3.3 Inductively Coupled Plasma</td>
<td>49</td>
</tr>
<tr>
<td>3.3.4 Differential Thermal Analysis</td>
<td>49</td>
</tr>
<tr>
<td>3.3.5 X-ray Photoelectron Spectroscopy (XPS)</td>
<td>50</td>
</tr>
<tr>
<td>3.3.6 Mössbauer Spectroscopy</td>
<td>51</td>
</tr>
<tr>
<td>3.3.7 Neutron Powder Diffraction (NPD) and Rietveld Refinements</td>
<td>51</td>
</tr>
</tbody>
</table>
3.4 Results and Discussion

3.4.1 Determination of Phase Purity

3.4.2 Oxidation State Determination

3.4.3 Verification of the Site Occupancy of Iron

3.4.4 Band Gap Estimation

3.5 Conclusion

3.6 References

4. Structure-Property Relationships Along the Fe-substituted CuInS$_2$ Series: Tuning of the Thermoelectric and Magnetic Properties

4.1 Introduction

4.2 Experimental

4.2.1 Reagents

4.2.2 Synthesis

4.2.3 Neutron Powder Diffraction and Rietveld Refinement

4.2.4 Synchrotron and Rietveld Refinement

4.2.5 Sample Densification and Determination of Sample Density

4.2.6 Thermal Conductivity

4.2.7 Thermopower and Electrical Conductivity

4.2.8 Magnetic Measurements

4.3 Results & Discussion

4.3.1 Neutron Powder Diffraction, Synchrotron Powder Diffraction, and Rietveld Refinement

4.3.2 Thermoelectric Properties
4.3.3 Magnetic Properties

4.4 Conclusions

4.5 References

5 Tuning the Band Gap of CuInS$_2$ Through Lithium and Iron Substitution

5.1 Introduction

5.2 Experimental

5.2.1 Reagents

5.2.2 Synthesis

5.2.3 X-ray Powder Diffraction and Rietveld Refinement

5.2.4 Optical Diffuse Reflectance UV/Vis/NIR Spectroscopy

5.2.5 Inductively Coupled Plasma

5.3 Results & Discussion

5.3.1 X-Ray Powder Diffraction and Rietveld Refinement

5.3.2 Band Gaps

5.4 Conclusion

5.5 References

6 Conclusions

6.1 Major Contributions

6.2 Comparison to Previous Studies

6.3 Future Directions

6.4 References
Table 1.1: Thermoelectric properties of select diamond-like semiconductors. T = temperature, σ = electrical conductivity, S = Seebeck coefficient, κ = thermal conductivity, ZT = dimensionless figure of merit for thermoelectric materials. Undoped materials in bold……………………………………………………………………11

Table 2.1: Summary of Mössbauer spectroscopy analysis of various iron containing Minerals, reproduced from reference 81.

DraytonMontmorillonite = (Ca_{0.27})(Si_{3.49}Al_{0.51})(Fe_{0.49}Al_{0.94}Mg_{0.82}Ti_{0.01}),
Muloorinaillite = (Ca_{0.059}K_{0.655})(Si_{3.597}Al_{0.403})(Fe_{0.628}Al_{0.969}Mg_{0.420}),
Francosia Glauconite = (Ca_{0.096}K_{0.725})(Si_{3.611}Al_{0.389})(Fe_{1.097}Al_{0.849}Mg_{0.442}Ti_{0.003}Mn_{0.004}),
Fiji Glauconite = (Ca_{0.076}K_{0.779})(Si_{3.836}Al_{0.112}Fe_{0.051})(Fe_{1.345}Mg_{0.595}Mn_{0.004})………………29

Table 3.1: Chemical composition of CuIn_{1-x}Fe_{x}S_{2}, where x = 0.05 - 0.15, measured by ICP. These formulae are normalized using the expected indium content…………………56

Table 3.2: PXRD Rietveld refinement details for CuIn_{1-x}Fe_{x}S_{2}, where x = 0.05 - 0.20..56

Table 3.3: XPS results for CuIn_{1-x}Fe_{x}S_{2}, where x = 0 - 0.15…………………60

Table 3.4: Mössbauer parameters for CuIn_{1-x}Fe_{x}S_{2}. I.S. - Isomer shift (relative to the source); Q.S. - Quadrupole splitting……………………………………64
Table 3.5: NPD Rietveld refinement details for CuIn$_{1-x}$Fe$_x$S$_2$, where x = 0.15………….66

Table 4.1: Powder and pellet densities of CuIn$_{1-x}$Fe$_x$S$_2$ (x = 0 - 0.15). The standard deviations appear in parentheses………………………………………………………………………….80

Table 4.2: Rietveld refinement results for neutron(N) and synchrotron(S) data from CuIn$_{1-x}$Fe$_x$S$_2$, where x = 0- 0.15…………………………………………………………………………83

Table 4.3: Thermoelectric properties of select diamond-like semiconductors. T = temperature, $\sigma$ = electrical conductivity, S = Seebeck coefficient, $\kappa$ = thermal conductivity, ZT = dimensionless figure of merit for thermoelectric………………….96

Table 4.4: The Weiss temperature, $\theta$, effective magnetic moment, $\mu_{\text{eff}}$, and Curie constant, C, for CuIn$_{1-x}$Fe$_x$S$_2$…………………………………………………………………………105

Table 5.1: Rietveld refinement results for X-ray powder diffraction data obtained for Cu$_{1-x}$Li$_x$InS$_2$, where x = 0-0.30…………………………………………………………………………121

Table 5.2: Rietveld refinement results for X-ray powder diffraction data from Cu$_{1-x}$Li$_x$In$_{0.90}$Fe$_{0.10}$S$_2$, where x = 0- 0.30…………………………………………………………………………123

Table 5.3: Chemical composition of Cu$_{1-x}$Li$_x$InS$_2$ and Cu$_{1-x}$Li$_x$In$_{0.90}$Fe$_{0.10}$S$_2$, where x = 0.10 - 0.30, measured by ICP. These formulae are normalized using the expected sulfur content…………………………………………………………………………124
Table 5.4: Bond distances generated from Rietveld refinement models………………132

Table 5.5: Summary of estimated band gaps from optical diffuse reflectance experiments….………………………………………………………………………………………………..134
LIST OF FIGURES

Figure 1.1: Cation substitution schematic for DLSs, adapted from a schematic, with permission, from ©2009 IEEE ................................................................. 2

Figure 1.2: Examples of the progression of cubic diamond-like structures ........... 3

Figure 1.3: A typical solar cell construct, used with permission from Dr. Michael Yakushev, Strathclyde University ................................................................. 6

Figure 1.4: Typical thermoelectric device ............................................................. 10

Figure 2.1: A. Surface of Fe metal before sputtering. B. Surface of Fe metal after sputtering for 5 mi. Adapted from a figure in reference 72, with permission from ©IOP Publishing ................................................................. 23

Figure 2.2: A. Surface of Fe$_3$O$_4$ before sputtering. B. 1 min. sputtering. C. 5 min. sputtering. D. 15 min. sputtering. E. 60 min. sputtering. Adapted from a figure in reference 72, with permission from ©IOP Publishing ................................................................. 24

Figure 2.3: Mössbauer spectra of iron doped CuCrS$_2$, 2% Fe(1), 3% Fe(2), 5% Fe(3), 15% Fe(4). Photos obtained from reference 82, with permission ......................... 30
Figure 2.4: Above left, the linear accelerator at the SNS, ORNL. Above right, the accumulator ring at the SNS, ORNL. Photos obtained from reference 82, with permission.

Figure 2.5: Above left, the liquid mercury target at the SNS, ORNL. Above right, the sample changer for POWGEN at the SNS, ORNL. Photos obtained from reference 82.

Figure 2.6: Penetration depth of neutron versus X-rays and electrons, Figure adapted from reference 83.

Figure 3.1: Left: The structure of a zinc blende double unit cell as viewed down the crystallographic b-axis. (purple = zinc, yellow = sulfur) Right: The structure of CuInS$_2$, I-42d, as viewed down the crystallographic b-axis. (green = copper, red = indium, yellow = sulfur).

Figure 3.2: Differential thermal analysis thermograms for CuIn$_{1-x}$Fe$_x$S$_2$ where top: $x=0$ and bottom: $x=0.15$. The heating curves are in red and the cooling curves in blue, with peak temperatures reported for each transition. Exothermic events point upward, and endothermic events point down.

Figure 3.3: X-ray powder diffraction patterns for CuIn$_{1-x}$Fe$_x$S$_2$, where $x = 0$ (JCPDS # 01-085-1575), 0.05, 0.075, 0.10, 0.125, and 0.15. The $(hkl)$ of the low intensity peaks.
were not labeled in order to improve clarity; all peaks can be indexed to the chalcopyrite structure.

Figure 3.4: Difference plot generated by the Rietveld refinement of XRPD data from CuIn$_{0.875}$Fe$_{0.125}$S$_2$ ($wR_p=0.0563$, $R_p=0.0424$, $\chi^2=1.989$). Observed (+++) and calculated (solid line) X-ray powder diffraction patterns are on top. The difference is shown on the bottom. The 2 sets of tick marks indicate the expected Bragg reflections of the sample and the Si standard, from top to bottom respectively.

Figure 3.5: Top: Refined lattice parameters, a (triangle) and c (open circle), for CuIn$_{1-x}$Fe$_x$S$_2$, where $x = 0.05$-$0.20$, versus iron concentration. Bottom: Refined unit cell volume for CuIn$_{1-x}$Fe$_x$S$_2$, where $x = 0.05$-$0.20$, versus iron concentration. The lines are a linear fit to the data for $x = 0.05$ to 0.15, as those above this concentration break the trend. Note that the error bars are omitted as they were not distinguishable from the data point markers.

Figure 3.6: XPS spectra for CuInS$_2$(top) and CuIn$_{0.85}$Fe$_{0.15}$S$_2$(bottom) for Cu 2$p_{3/2}$, Cu 2$p_{1/2}$, In 3$d_{3/2}$, In 3$d_{5/2}$, S 2$p_{3/2}$, S 2$p_{1/2}$.

Figure 3.7: Mössbauer spectra for a) CuIn$_{0.90}$Fe$_{0.10}$S$_2$, b) CuIn$_{0.875}$Fe$_{0.125}$S$_2$, and c) CuIn$_{0.85}$Fe$_{0.15}$S$_2$. The green and blue peaks indicate the separate peaks fitted to the data, while the red peak indicates the sum of these peaks.
Figure 3.8: Difference plot generated by the Rietveld refinement of NPD data from CuIn$_{0.85}$Fe$_{0.15}$S$_2$ ($wR_p = 0.0192$, $R_p = 0.0335$, $\chi^2 = 1.736$). Observed (+++) and calculated (solid line) neutron diffraction patterns are on top. The difference is shown in the blue plot on the bottom. The 2 sets of tick marks indicate the Bragg reflections of the vanadium sample holder and the sample from top to bottom respectively.

Figure 3.9: Diffuse reflectance spectra for CuIn$_{1-x}$Fe$_x$S$_2$ where, for clarity $x = 0$, $x = 0.05$, and $x = 0.075$ are shown.

Figure 4.1: The crystal structure of CuInS$_2$ (I-42d), as viewed down the crystallographic $b$-axis.

Figure 4.2: Neutron powder diffraction data difference plot for CuIn$_{1-x}$Fe$_x$S$_2$, Top: $x = 0.125$ and Bottom: $x = 0.15$, generated by Rietveld refinement. Observed (+++) and calculated (solid line) neutron diffraction patterns are on top in each plot. The difference is shown on the bottom. The tick marks indicate the expected Bragg reflections of the sample. The bottom inset shows the magnification of the largest unindexed peak for $x = 0.15$.

Figure 4.3: Synchrotron powder diffraction data difference plot for CuIn$_{1-x}$Fe$_x$S$_2$, Top: $x = 0.125$ and Bottom: $x = 0.15$, generated by Rietveld refinement. Observed (+++) and calculated (solid line) synchrotron diffraction patterns are on top in each plot. The difference is shown on the bottom. The tick marks indicate the expected Bragg reflections.
Figure 4.4: Electrical conductivity of CuInS$_2$ (▲), CuIn$_{0.90}$Fe$_{0.10}$S$_2$ (●), CuIn$_{0.875}$Fe$_{0.125}$S$_2$ (▼) and CuIn$_{0.85}$Fe$_{0.15}$S$_2$ (■)…………………………………………………………………………………87

Figure 4.5: Temperature dependence of Seebeck coefficient for CuInS$_2$ (▲), CuIn$_{0.90}$Fe$_{0.10}$S$_2$ (●), CuIn$_{0.875}$Fe$_{0.125}$S$_2$ (▼) and CuIn$_{0.85}$Fe$_{0.15}$S$_2$ (■)………………………………92

Figure 4.6: Thermal conductivity and lattice thermal conductivity (inset) as a function of temperature for CuInS$_2$ (▲), CuIn$_{0.90}$Fe$_{0.10}$S$_2$ (●), CuIn$_{0.875}$Fe$_{0.125}$S$_2$ (▼) and CuIn$_{0.85}$Fe$_{0.15}$S$_2$ (■)……………………………………………………………………………94

Figure 4.7: The thermoelectric figure of merit, ZT, as a function of temperature for CuInS$_2$ (▲), CuIn$_{0.90}$Fe$_{0.10}$S$_2$ (●), CuIn$_{0.875}$Fe$_{0.125}$S$_2$ (▼) and CuIn$_{0.85}$Fe$_{0.15}$S$_2$ (■)………97

Figure 4.8: Temperature dependence of magnetic susceptibility of CuIn$_{0.9}$Fe$_{0.1}$S$_2$ at 100 Oe under ZTC conditions. The inset shows the temperature dependence of the magnetic susceptibility measured under ZFC and FC conditions at an applied field of 100 Oe….99

Figure 4.9: Top: Temperature dependence of magnetic susceptibility of CuIn$_{0.875}$Fe$_{0.125}$S$_2$ at 100 Oe under ZFC conditions. The insets shows the temperature dependence of the magnetic susceptibility measured under ZFC and FC conditions at an applied field of 100
Oe Bottom: Temperature dependence of magnetic susceptibility of CuIn$_{0.85}$Fe$_{0.15}$S$_2$ at 100 Oe. The insets show the temperature dependence of the magnetic susceptibility measured under ZFC and FC conditions at an applied field of 100 Oe.

Figure 4.10: $\chi^T$ vs. temperature plot for CuIn$_{0.875}$Fe$_{0.125}$S$_2$ (Top) and CuIn$_{0.85}$Fe$_{0.15}$S$_2$ (Bottom)

Figure 4.11: Top: Field dependence of the magnetization of CuIn$_{0.85}$Fe$_{0.15}$S$_2$ measured at 2 K. The inset shows -0.5 to 0.5 T range. Bottom: Field dependence of the magnetization of CuIn$_{0.875}$Fe$_{0.125}$S$_2$ measured at 2 K. The inset shows -0.3 to 0.3 T range.

Figure 5.1: Left: CuInS$_2$, I-42d structure as viewed down the crystallographic b-axis. Right: Li$_2$FeS$_2$, P-3m1 structure as viewed down the crystallographic b-axis.

Figure 5.2: Heating profile for both Cu$_{1-x}$Li$_x$InS$_2$ and Cu$_{1-x}$Li$_x$In$_{0.90}$Fe$_{0.10}$S$_2$ series.

Figure 5.3: Rietveld refinement results using X-ray powder diffraction data for Cu$_{1-x}$Li$_x$InS$_2$ Observed (+++) and calculated (red solid line) X-ray powder diffraction patterns are on top. The difference is shown in the plot on the bottom. The two sets of tick marks indicate the expected Bragg reflections of Si and the refined model.

Figure 5.4: Rietveld refinement results using X-ray powder diffraction data for Cu$_{1-x}$Li$_x$In$_{0.90}$Fe$_{0.10}$S$_2$ Observed (+++) and calculated (red solid line) X-ray powder diffraction patterns are on top. The difference is shown in the plot on the bottom. The two sets of tick marks indicate the expected Bragg reflections of Si and the refined model.
diffraction patterns are on top. The difference is shown in the plot on the bottom. The
two sets of tick marks indicate the expected Bragg reflections of Si and the refined
model………………………………………………………………………………………………………………………125

Figure 5.5: Top: Refined lattice parameter $a$ for both $\text{Cu}_{1-x}\text{Li}_x\text{InS}_2$ and
$\text{Cu}_{1-x}\text{Li}_x\text{In}_{0.90}\text{Fe}_{0.10}\text{S}_2$, where $x = 0.05$-0.30, versus lithium concentration. Bottom:
Refined lattice parameter $c$ for both $\text{Cu}_{1-x}\text{Li}_x\text{InS}_2$ and $\text{Cu}_{1-x}\text{Li}_x\text{In}_{0.90}\text{Fe}_{0.10}\text{S}_2$, where $x = 0.05$-0.30. Note that the error bars are omitted as they were not distinguishable from the
data point markers…………………………………………………………………………………………………………126

Figure 5.6: The $c/a$ ratio vs lithium content for both series, $\text{Cu}_{1-x}\text{Li}_x\text{InS}_2$ and
$\text{Cu}_{1-x}\text{Li}_x\text{In}_{0.90}\text{Fe}_{0.10}\text{S}_2$, where $x = 0.05$-0.30. The data point for the $x = 0.20$ samples are
nearly on top of one another…………………………………………………………………………………………………128

Figure 5.7: Refined cell volumes for both $\text{Cu}_{1-x}\text{Li}_x\text{InS}_2$ and $\text{Cu}_{1-x}\text{Li}_x\text{In}_{0.90}\text{Fe}_{0.10}\text{S}_2$, where $x = 0.05$-0.30, versus lithium concentration. Note that the error bars are omitted as they
were not distinguishable from the data point markers……………………………………………………………………129

Figure 5.8: Top: Depiction of band structure and band gap variation of $\text{CuInS}_2$ with Fe-
and Li-substitution. Bottom: Bond alternation in $\text{CuInS}_2$ with and corresponding changes
in $x_s$. CB min, VB max, and IB refer to the minimum conduction band, maximum
valence band, and intermediate band respectively………………………………………………………………130
Figure 5.9: Optical diffuse reflectance spectra converted to absorption for Cu$_{1-x}$Li$_x$InS$_2$, where $x = 0 – 0.30$. ……………………………………………………………………………………………………….134

Figure 5.10: Optical diffuse reflectance spectra converted to absorption for Cu$_{1-x}$Li$_x$In$_{0.90}$Fe$_{0.10}$S$_2$, where $x = 0 – 0.30$. ……………………………………………………………………………………………………….137
1. An Introduction to Diamond-Like Semiconductors

1.1 Introduction

Alternative sources of energy are constantly being sought after to decrease reliance on fossil fuels. Renewable energy sources, such as solar and wind, are being aggressively studied. Thermoelectric devices are another highly desirable alternative energy source, as devices exhibiting the Seebeck effect can be used to generate electricity from waste heat. Many promising photovoltaic and thermoelectric materials are diamond-like semiconductors (DLSs). The physicochemical properties of DLSs often times can be tuned with the addition of a dopant.

In hopes of one day being able to predict the effects of doping on the physical properties of a material, it is imperative to study the structure-property relationships of these materials. The hypothesis of this work is that the doping of CuInS₂ with iron and/or lithium, will elicit property changes. The specific aims of this research project are: (1) To determine the solubility limit of Fe in place of In in CuInS₂, and determine the oxidation states and location of all of the elemental constituents, as well as measuring the band gap of the solid solutions as a function of the dopant concentration, (2) to measure the magnetic and thermoelectric properties of the Fe-substituted materials and complete a thorough structural study in order to explore structure-property relationships, (3) and to determine the solubility limit of Li in place of Cu in both the CuInS₂ system and the CuIn₀.₉Fe₀.₁S₂ system, as well as measuring the band gap of the solid solution members as a function of the dopant concentration. This research has the potential to bring us closer
to the realization of new materials that may have promising photovoltaic, thermoelectric, and magnetic applications.

1.2 Fundamentals of Diamond-Like Semiconductors

Diamond-like semiconductors are an attractive class of compounds to pursue owing to the flexibility of their composition. DLS have crystal structures that are related to either the cubic or hexagonal forms of diamond. In these structures half of the carbon sites are occupied with anions and the other half are occupied by cations. ZnS, for

Figure 1.1: Cation substitution schematic for DLSs, adapted from a schematic, with permission, from ©2009 IEEE.
example, crystallizes both in the sphalerite structure type, which is derived from the cubic diamond structure, and the wurtzite structure type, which is derived from the hexagonal diamond structure. The mental construct of cation cross-substitutions can lead to ternary and quaternary diamond-like semiconductors (Fig: 1.1, 1.2). CuAlS$_2$ and Cu$_2$ZnGeS$_4$ are just two of many examples of these semiconductors.

![Cubic Diamond](image1)

**Figure 1.2: Examples of the progression of cubic diamond-like structures.**

There are four rules that a material should follow to be considered a DLS. The first rule is that the average valence electron concentration must be 4. The second rule is that the average number of valence electrons per anion must be 8. The third rule is that all of the ions in the structure must be tetrahedral. Pauling’s first rule, the radius ratio rule, is often used as a guideline in the prediction of tetrahedral coordination. The fourth
rule is that Pauling’s second rule should be satisfied.\textsuperscript{4} This rule, known as the electrostatic valence sum rule, states that each anion must have its octet satisfied by the cations in its immediate coordination sphere. Following these rules, a large but finite series of compounds can be created where the resulting physicochemical properties will depend on the composition and cation ordering of the materials. DLS materials have a wide variety of applications from light emitting diodes,\textsuperscript{5} spintronics,\textsuperscript{6,7} thermoelectric devices,\textsuperscript{8} nonlinear optical materials,\textsuperscript{10} to photovoltaic applications, etc.\textsuperscript{1}

1.3 Introduction to Photovoltaics

Currently, solar energy is being used to power a multitude of devices from calculators to space satellites. Photovoltaic devices, however, are neither efficient nor sufficiently cost-effective to replace a large portion of the fossil-fuel-based energy production. CuInS\textsubscript{2}-based compounds are promising photovoltaic materials because they have high absorption coefficients of $\sim10^5\text{cm}^{-1}$, and are direct band gap semiconductors with a band gap ($\sim1.5$ eV) that is close to optimal for use as the absorber layer in solar cells.\textsuperscript{11,12} The increasing cost and decreasing availability of indium, however, makes it a less desirable substituent in these materials. This project explores the substitution of indium with iron, which is both readily available and much less expensive. Previous studies have suggested that the substitution of Fe for In will lower the band gap of the material below the desirable range for photovoltaic use.\textsuperscript{13,14} Thus the exploration of codoping with lithium, in hopes of being able to tune the band gap, is an attractive prospect.
1.31 Photovoltaic Cells

Photovoltaic cells are being widely researched as a tool to harness the sun’s energy. This provides an alternative energy source to fossil-fuel-based energy. However, a decrease in material and production cost and/or an increase in efficiency is necessary to make photovoltaic energy a reasonable substitution for current energy sources.\textsuperscript{15} As of 2009, photovoltaic cells of polycrystalline silicon, a diamond-like semiconductor, are more than twice the cost of natural gas and wind. Nonsilicon-based photovoltaic materials such as thin films of \text{Cu(InGa)Se}_2, a diamond-like semiconductor, offer a cost reduction and an increase in efficiency; however the supply of indium is a concern.\textsuperscript{16,15} Goetzberger, Hebling, and Schock state that the requirements for an ideal solar cell material are: a band gap between 1.1 eV – 1.7 eV, direct band structure, consists of readily available and non-toxic materials, reproducible deposition technique, long term stability, and good photovoltaic conversion efficiency.\textsuperscript{17}

A thin film solar cell is comprised of several layers (Fig: 1.3). The top most layer usually consists of a transparent conducting oxide (TCO) that allows solar light to pass through, without allowing it to reflect back out of the film. Once the light passes through the TCO it continues to pass through the next layer, which is the window layer. The window layer, or emitter layer, consists of an n-type material such as \text{CdS}. The absorber layer is a p-type material, such as \text{CuInS}_2, that has the ability to absorb photons and generate an electron hole pair. The hole transports to the backside metal contact, which is often molybdenum. The electron ejects across the p-n junction, and across the emitter to the front side contact made of a material such as nickel or aluminum. This process is what creates the current. The entire film is usually built on a glass substrate. Soda lime
glass is often used because it has been noted\textsuperscript{18} that the sodium from the substrate serves as a source of dopant for the absorber layer, which in turn increases the efficiency of the solar cell.\textsuperscript{15} The focus of this research is primarily on the absorber layer which is typically a diamond-like semiconductor.

![Diagram of a typical solar cell construct](image)

**Figure 1.3:** A typical solar cell construct, used with permission from Dr. Michael Yakushev, Strathclyde University.\textsuperscript{19}

### 1.32 Diamond-Like Semiconductors of Current Interest For Photovoltaic Applications

Silicon cells have historically been the standard photovoltaic material. CuInSe\textsubscript{2} (CIS) and CuInS\textsubscript{2} (CISU) are two interesting photovoltaic materials that are diamond-like semiconductors. Unlike silicon, CIS and CISU have direct band gaps. The CIS cells have been found to be so promising that as of 2007, there were 9 commercial companies
producing CIS photovoltaic products. CuInSe$_2$ has a reported band gap of 1.02-1.04 eV$^{20}$ and is used as an absorber layer in solar cells. CuInS$_2$, with a band gap of 1.52-1.55 eV$^{21}$, unlike CuInSe$_2$ lies within the optimal band gap range for photovoltaic devices (1.1-1.7 eV).$^{17}$ However, the solar cell efficiency is lower because of difficulties during production, specifically related to the control of sulfur during deposition.$^{2,22}$ As a means of band gap engineering, many different solid solutions are being explored such as Cu(In,Ga)Se$_2$ (CIGS), Cu(In,Ga)$_2$S$_2$, and Cu(In,Al)$_2$Se$_2$. CIGS cells have measured efficiencies as high as 21.8% ±1.5.$^{26}$

### 1.33 Targeting New DLSs With Photovoltaic Applications

Major concerns for CIS photovoltaic production are cost, future availability of material, and efficiency. Even assuming a 70% recovery factor, it is estimated that indium may be mined out in 66 yrs.$^1$ The research reported here is focused on substituting the indium in CuInS$_2$ with iron, a much cheaper and more readily available element. The doping of CIS and CISU is not a novel idea. However the majority of studies look at substituting a minimal amount of another element in order to elicit a property change. Few of these studies are in order to replace a significant amount of an element. The doping and synthesis of solid state solutions of CuInSe$_2$ have historically been performed in order to study the effects on the unit cell parameters, band gap, electrical properties, among other properties.$^{27}$ Co,$^{27}$ Cd,$^{28}$ Zn,$^{29}$ Mg,$^{27}$ Cl,$^{28}$ Br,$^{27}$ I,$^{27}$ V,$^{30}$ and O$_2$,$^{31}$ are many of the dopants that have been added to CIS.$^{32}$ The focus of the research on Co and Zn has primarily been that of studying the phases attained with changing the amount of dopant.$^{27,29}$ Cd, Mg, Cl, and Br have been shown to be
successful \textit{n}-type dopants.\textsuperscript{27,28} The doping of CuInSe\textsubscript{2} with oxygen was found to increase the unit cell volume and decrease the band gap.\textsuperscript{31}

The doping of CIS\textsubscript{U} has also been widely studied. The focus is primarily the same as that of the doping of CIS. Some of the dopants that have been studied are Cd,\textsuperscript{33} Na,\textsuperscript{34,35} N,\textsuperscript{36} P,\textsuperscript{37} As,\textsuperscript{38} Sb,\textsuperscript{39} Bi,\textsuperscript{40} Yb,\textsuperscript{41} Zn,\textsuperscript{39} and Ga.\textsuperscript{35} Sodium doping has been studied and has been found to increase the efficiency of solar cells.\textsuperscript{34,35} Arsenic, nitrogen, and cadmium doping has only been studied theoretically with a focus on enhancing the \textit{p}-type conductivity.\textsuperscript{33,36,38} The effects of doping on conductivity and bandgap have been conducted using P,\textsuperscript{35} Sb,\textsuperscript{37} Bi,\textsuperscript{39} Yb,\textsuperscript{40} Zn,\textsuperscript{41} and Ga. Other substitutions should be explored and systematic approaches should be applied to these studies.

1.4 Introduction to Thermoelectrics (TEs)

Thermoelectric (TE) devices are employed as thermocyclers in DNA synthesis, car seat heaters/coolers, laser diodes, portable picnic coolers, and small power generation modules.\textsuperscript{42,43,44,45} These devices are desirable as they eliminate the need for gas or fluid refrigerants such as hydrochlorofluorocarbons (HCICs) and chlorofluorocarbons (CFCs). The finished TE devices are usually quite small and have no moving parts that need regular maintenance and/or repair. The solid-state energy converters help to reduce ozone depletion, green house gas emission, and fossil fuel usage.\textsuperscript{48} Why then are these devices not more widely used? The lack of efficiency is the primary reason. To characterize the thermoelectric efficiency of a material, ZT is employed. $ZT = \sigma S^2 T / \kappa_{Tot}$, where $\sigma$ is the electrical conductivity, $S$ is the Seebeck coefficient, $T$ is the absolute temperature, and $\kappa_{Tot}$ is the total thermal conductivity, comprised of both the electronic
thermal conductivity ($\kappa_e$) and the lattice thermal conductivity ($\kappa_L$). The current thermoelectric devices have a ZT (dimensionless figure of merit) around 1. It is estimated that an average ZT between 1.5-2 is sufficient to employ thermoelectric devices into a broader spectrum of products.\textsuperscript{48,49} To be able to employ the use of thermoelectric devices in home refrigeration, it is estimated that a ZT = 4 would be necessary.\textsuperscript{49} Recently, DLSs such as CuInTe\textsubscript{2} and Cu\textsubscript{2}Sn\textsubscript{1-x}In\textsubscript{x}Se\textsubscript{3} have attracted much attention for their thermoelectric properties.\textsuperscript{46,47} Previous studies have also shown that the doping of DLSs have enhanced the ZT values of the materials (Table 1.1), to this end it is wise to explore the thermoelectric properties of the solid solutions synthesized in this work.

1.41 Thermoelectric Devices

Thermoelectric devices are considered to be solid state energy converters.\textsuperscript{48} There are two types of thermoelectric devices, one exhibiting the Peltier effect, and the other the Seebeck effect (Fig. 4).\textsuperscript{49} The Peltier effect is that in which electricity is used to generate a temperature gradient. The devices consist of $p$-type and $n$-type semiconductors (often doped) connected by conducting shunts, typically made of copper.\textsuperscript{48} As can be seen in Figure 4, when a current is applied, the current flows from the $n$-type material to the $p$-type, and the dominant carriers in both materials carry away heat as they move away from the junction. The junction then becomes cold as the electrical current carries the heat away. These devices can be used in refrigeration.\textsuperscript{48,49}
Figure 1.4: Typical thermoelectric device.

The thermoelectric devices that are driven by the Seebeck effect, convert heat into electricity. The devices are constructed in the same manner as the Peltier devices however, when a temperature gradient is applied, electricity is generated (Figure 1.4). Heat is transported by the flow of the dominant carriers, from the junction to the base.
Table 1.1: Thermoelectric properties of select diamond-like semiconductors. T = temperature, σ = electrical conductivity, S = Seebeck coefficient, κ = thermal conductivity, ZT = dimensionless figure of merit for thermoelectric materials. Undoped materials in bold.

<table>
<thead>
<tr>
<th>Compound</th>
<th>T (K)</th>
<th>σ (Scm⁻¹)</th>
<th>S(μVK⁻¹) absolute</th>
<th>κ(Wm⁻¹K⁻¹)</th>
<th>ZT</th>
<th>Ref.</th>
</tr>
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<tbody>
<tr>
<td>Cu₂CdSnSe₄</td>
<td>700</td>
<td>31.3</td>
<td>298</td>
<td>1.01</td>
<td>1.9 x 10⁻¹</td>
<td>53</td>
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<td>Cu₂.025Cd.975SnSe₄</td>
<td>700</td>
<td>62.3</td>
<td>204</td>
<td>0.75</td>
<td>2.4 x 10⁻¹</td>
<td>53</td>
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<td>Cu₂.05Cd.95SnSe₄</td>
<td>700</td>
<td>142.5</td>
<td>171</td>
<td>0.61</td>
<td>4.8 x 10⁻¹</td>
<td>53</td>
</tr>
<tr>
<td>Cu₂.10Cd.80SnSe₄</td>
<td>700</td>
<td>189.5</td>
<td>156</td>
<td>0.49</td>
<td>6.5 x 10⁻¹</td>
<td>53</td>
</tr>
<tr>
<td>Cu₂ZnSnS₄</td>
<td>700</td>
<td>5.3</td>
<td>355</td>
<td>1.21</td>
<td>3.9 x 10⁻²</td>
<td>54</td>
</tr>
<tr>
<td>Cu₂Zn₉₀Sn₃₄</td>
<td>700</td>
<td>131</td>
<td>211</td>
<td>1.12</td>
<td>3.6 x 10⁻¹</td>
<td>54</td>
</tr>
<tr>
<td>Cu₂Zn₉₀Sn₉₄</td>
<td>700</td>
<td>225</td>
<td>156</td>
<td>2.11</td>
<td>1.8 x 10⁻¹</td>
<td>54</td>
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<tr>
<td>Cu₂.10Zn₉₀Sn₃₄</td>
<td>700</td>
<td>810</td>
<td>112</td>
<td>1.55</td>
<td>4.5 x 10⁻¹</td>
<td>54</td>
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<td>Cu₂.10Zn₈₅Inₙ₃Sn₄</td>
<td>860</td>
<td>332</td>
<td>202</td>
<td>1.28</td>
<td>9.1 x 10⁻¹</td>
<td>54</td>
</tr>
<tr>
<td>Cu₂ZnSn₈₅Inₙ₃Sn₄</td>
<td>700</td>
<td>165</td>
<td>197</td>
<td>1.34</td>
<td>3.3 x 10⁻¹</td>
<td>55</td>
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<tr>
<td>CuInSe₃</td>
<td>560</td>
<td>0.09</td>
<td>206</td>
<td>1.9</td>
<td>1.1 x 10⁻⁴</td>
<td>56</td>
</tr>
<tr>
<td>CuIn₉₅Mn₉₅Se₂</td>
<td>560</td>
<td>2.9</td>
<td>424</td>
<td>1.8</td>
<td>1.6 x 10⁻²</td>
<td>56</td>
</tr>
<tr>
<td>CuIn₉₀Mn₉₀Se₂</td>
<td>560</td>
<td>2.2</td>
<td>480</td>
<td>1.8</td>
<td>1.4 x 10⁻²</td>
<td>56</td>
</tr>
<tr>
<td>Cu₉₀In₉₀Mn₉₀Se₂</td>
<td>560</td>
<td>1.4</td>
<td>551</td>
<td>1.6</td>
<td>1.4 x 10⁻²</td>
<td>56</td>
</tr>
<tr>
<td>Cu₂SnSe₃</td>
<td>850</td>
<td>108</td>
<td>~229</td>
<td>~0.9</td>
<td>5.0 x 10⁻¹</td>
<td>47</td>
</tr>
<tr>
<td>Cu₅Sn₄In₉₃Se₅</td>
<td>850</td>
<td>~278</td>
<td>~208</td>
<td>~0.9</td>
<td>1.14</td>
<td>47</td>
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<tr>
<td>Cu₁₄Fe₁₉S₃₃(x=0.05)</td>
<td>300</td>
<td>~111</td>
<td>~185</td>
<td>~3.61</td>
<td>~3.2 x 10⁻²</td>
<td>57</td>
</tr>
<tr>
<td>CuInTe₃ (annealed 7 days)</td>
<td>850</td>
<td>~173</td>
<td>~283</td>
<td>~1.0</td>
<td>1.18</td>
<td>46</td>
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<tr>
<td>Cu₀.₄InTe₂</td>
<td>702</td>
<td>~14.2</td>
<td>~310</td>
<td>~0.54</td>
<td>0.17</td>
<td>58</td>
</tr>
<tr>
<td>CuGaTe₂</td>
<td>950</td>
<td>227</td>
<td>244</td>
<td>~0.89</td>
<td>1.4</td>
<td>62</td>
</tr>
<tr>
<td>Cu₁₄GaSb₂₇Te₂(x=0.02)</td>
<td>721</td>
<td>~156</td>
<td>~262</td>
<td>~0.72</td>
<td>1.07</td>
<td>61</td>
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<td>Cu₅Sb₉₅Sn₉₂₅Se₄</td>
<td>673</td>
<td>~229</td>
<td>~238</td>
<td>~1.16</td>
<td>0.75</td>
<td>59</td>
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<tr>
<td>AgInSe₂</td>
<td>724</td>
<td>~7.6</td>
<td>~470</td>
<td>~0.35</td>
<td>0.34</td>
<td>60</td>
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<td>Cu₂Mn₀.₃Sn₉₉Se₇</td>
<td>715</td>
<td>~695</td>
<td>~114</td>
<td>~1.59</td>
<td>0.41</td>
<td>50</td>
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<tr>
<td>Cu₂Mn₀.₅Sn₉₈Se₇</td>
<td>715</td>
<td>~726</td>
<td>~111</td>
<td>~1.89</td>
<td>0.34</td>
<td>50</td>
</tr>
<tr>
<td>Cu₂Mn₀.₅Sn₉₅Se₇</td>
<td>715</td>
<td>~1161</td>
<td>~83.1</td>
<td>~2.12</td>
<td>0.27</td>
<td>50</td>
</tr>
<tr>
<td>Cu₃GeSe₃</td>
<td>745</td>
<td>~11.78</td>
<td>446</td>
<td>0.67</td>
<td>0.28</td>
<td>51</td>
</tr>
<tr>
<td>Cu₅Ga₀.₇₃Ge₀.₂₇Se₃</td>
<td>745</td>
<td>~368</td>
<td>~150</td>
<td>~1.38</td>
<td>0.50</td>
<td>51</td>
</tr>
</tbody>
</table>

This generates a voltage between the two ends of the device.⁴⁸,⁴⁹ These devices are suited to generate electricity from waste heat, such as that produced in an industrial setting or from the exhaust of a car.⁴⁸,⁴⁹ Unfortunately, these small, relatively inexpensive, and
environmentally friendly devices have not reached an efficiency great enough to be more widely used.\textsuperscript{49}

### 1.42 Targeting New DLSs With Thermoelectric Applications

Most commercial thermoelectric devices are constructed from Bi\textsubscript{2}Te\textsubscript{3}-based materials.\textsuperscript{52} There are diamond-like semiconductors that are now achieving ZT’s that are comparable to these compounds. These materials include quaternary and ternary DLS, both doped and undoped (Table 1.1).\textsuperscript{53,54,55,56,57,58,59,60} Some of the most promising compounds are Cu\textsubscript{2}Sn\textsubscript{0.9}In\textsubscript{0.1}S\textsubscript{3} with a ZT = 1.14 at 850 K\textsuperscript{47}, Cu\textsubscript{0.9}GaSb\textsubscript{1}Te\textsubscript{2} with a ZT = 1.07 at 721 K\textsuperscript{61}, CuInTe\textsubscript{2} with a ZT = 1.18 at 850 K\textsuperscript{46}, and CuGaTe\textsubscript{2} with a ZT of 1.4 at 950 K (Table 1.1).\textsuperscript{62}

A promising approach to developing new thermoelectric bulk materials is to target small band gap semiconductors, and dope them heavily.\textsuperscript{49} This approach has been proven successful in systems such as Cu\textsubscript{2}Sn\textsubscript{0.9}In\textsubscript{0.1}S\textsubscript{3} and Cu\textsubscript{0.9}GaSb\textsubscript{1}Te\textsubscript{2}.\textsuperscript{47,61} Increasing the structural complexity in general can also enhance the ZT. This is a logical approach as it often decreases $\kappa$. However, in Cu\textsubscript{1-x}InTe\textsubscript{2} where $x = 0.4$, the $\kappa$ dramatically decreases, but so does the conductivity, resulting in a decrease in the ZT from 0.53 in the parent compound to 0.17 in the defect structure.\textsuperscript{58} In another study of CuInTe\textsubscript{2}, the ZT of the undoped material is 1.18.\textsuperscript{46} This disparity in ZT for the undoped compounds could be due to a secondary phase that appears to be present in the X-ray powder diffraction patterns of the material with the higher ZT,\textsuperscript{46} or it may be due to different synthetic routes, or even impurities in the starting materials.
In the Cu_{2+x}Cd_{1-x}SnSe_4, Cu_{2+x}Zn_{1-x}SnS_4, and Cu_{1-x}Fe_{1+x}S_2 systems, the compositional flexibility may add a structural complexity that results in an increase in ZT.\textsuperscript{57,63,64} As structural complexity increases, it increases the scattering of phonons, which in turn reduces the lattice thermal conductivity resulting in an increased ZT (assuming that all other factors remain unchanged). There are also undoped ternary systems with promising ZT’s such as CuGaTe_2, AgInSe_2, and CuInTe_2 that could prove to be very successful commercial thermoelectric candidates upon further exploration.\textsuperscript{62,65,46} However, much more research needs to be done in order to understand the structure-property relationships of these and other diamond-like semiconductors in order to successfully design future thermoelectric materials. Neutron and synchrotron powder diffraction can provide data for the necessary advanced structural analysis that will allow for a better understanding of the structure-property relationships.

1.5 Magnetic Properties

Although magnetism is not a major focus in this work, it cannot be ignored. Bruno Del Re’s magnetic study on Fe-substituted CuInS_2 revealed that even the samples thought to be phase pure by laboratory X-ray powder diffraction had a small, but present, secondary phase that contained Fe in the 2+ oxidation state.\textsuperscript{66} It was the Mössbauer analysis that revealed that both Fe^{2+} and Fe^{3+} are present in each of the samples, and as the amount of substitution increases, so does the amount of Fe^{2+}. This work then, is the first to analyze phase-pure Fe-substituted CuInS_2.

This work will explore the solubility limit of Fe for In in CuInS_2 with laboratory X-ray powder diffraction and high quality neutron and synchrotron powder diffraction.
The oxidation states and site occupancies for each of the constituent elements will be determined. The magnetic and thermoelectric properties of the Fe-substituted CuInS\textsubscript{2} series will also be investigated. The band gaps will then be estimated for this series. A Li-substituted CuInS\textsubscript{2} and CuIn\textsubscript{0.90}Fe\textsubscript{0.10}S\textsubscript{2} series will be synthesized and characterized with laboratory X-ray powder diffraction and the band gaps will also be estimated for these samples.
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[accessed 5/20/2013]


2. Materials Characterization

2.1 Introduction to Materials Characterization

Although DLSs are an extensively researched class of materials, much of the research is not systematic in nature and lacks in-depth structural analysis. Very few studies thoroughly characterize the material under investigation. For example, most studies of doped DLSs assume that the oxidation numbers of the constituents are the intended oxidation numbers. This work presents a systematic, thorough characterization of heavily doped CuInS$_2$. The solid solutions synthesized for this work are characterized using X-ray powder diffraction, time of flight neutron powder diffraction, synchrotron powder diffraction, differential thermal analysis, X-ray photoelectron spectroscopy, inductively coupled plasma, scanning electron microscopy, energy dispersive spectroscopy, Mössbauer spectroscopy, and diffuse reflectance UV/Vis/NIR spectroscopy. Thermal, electrical, and magnetic properties will also be presented.

Few studies of doped DLSs have verified the oxidation state of each constituent element, or verified in which crystallographic site(s) the dopant resides. In this work, the oxidation states are not assumed. Both X-ray photoelectron spectroscopy (XPS) and Mössbauer spectroscopy were employed to confirm the oxidation states of the constituent ions. Because these two techniques are not typically available in chemistry departments, and the interpretation of the data is often times not straightforward, they are explained in greater detail than the other, more common, characterization methods (which will be described later in this work).
An advanced structural analysis of the Fe-substituted materials in this study has been undertaken. High-quality synchrotron powder diffraction data, as well as neutron powder diffraction data were collected in this investigation. Details are provided in this chapter for the neutron diffraction study, as it has been conducted using a time of flight (TOF) neutron powder diffraction diffractometer which is rather unique and only found in a few national laboratories around the world. Thermoelectric measurements also play an important role in this research so some time will be spent discussing these techniques as they are also atypical for a chemistry department. The attention to details like oxidation state and site occupancy as well as the thorough characterization strategy, are some of the factors that contribute to making this work unique.

2.2 X-Ray Photoelectron Spectroscopy

In XPS, X-ray beams from either a monochromatic Al $\text{K}_\alpha$ or Mg $\text{K}_\alpha$ source are used to eject core electrons from the surface of a sample. The electrons that are ejected are detected, and the kinetic energy of the electron is measured. Kinetic energy can be converted to binding energy simply by subtracting the work function and the kinetic energy from the photon energy. The resulting spectrum is plotted as binding energy vs. cps. An electron’s binding energy is characteristic of the element and the orbital of origination. Changes in the environment of the electron (oxidation state or binding) will have an effect on the binding energy. For example, there will be an increase in binding energy if there is an increase in oxidation state (ie. Fe$^{2+}$ to Fe$^{3+}$). It is important to note, however, that XPS is a surface analysis tool, and cannot be used to study of the bulk sample.
There are several aspects of an XPS spectrum that need to be analyzed in order to determine the elements present, in addition to their respective oxidation states. XPS can also be used for elemental quantification; however, this application was not used for this work, as different elements can sputter at different rates, making it difficult to quantify the data. Referencing published values and databases, such as the NIST XPS data base, in order to determine the expected binding energy of an ion or element is essential. XPS is very sensitive to spin orbital splitting and auger electrons. It is very important to note that the binding energies of the \( p, d, \) and \( f \) orbitals are observed as two peaks as a result of spin orbital splitting. The location, separation of the two peaks, and the integral are compared with published values. The location of a peak represents the binding energy of the electron. The fact that the peaks that are indicative of a specific element or ion and that the peaks can also shift as a result of a change in local environment helps to determine what is chemically bound to the element. The ratio of peak integrals allows for their comparison, and the FWHM (full width at half maximum) of the peak can be measured to help distinguish between an ion’s nearest neighbors, as in Cho’s study, which compared various samples that include a metal that is coordinated to different ions.

In this work the determination of \( \text{Cu}^+ \) and \( \text{Fe}^{3+} \) is particularly challenging because of the similar binding energies for ions having different oxidation states, peak overlap, and reduction due to sputtering. Auger peaks and satellite peaks can be useful in the analysis of the data. Yao et al. notes that \( \text{Cu}^{2+} \) exhibits a higher binding energy satellite peak associated with the \( \text{Cu} \ 2p_{3/2} \) peak. The \( \text{Cu} 2p_{3/2} \) peak is often of a similar binding energy in both \( \text{Cu}^{2+} \) and \( \text{Cu}^{1+} \), so the satellite peak is often the discerning factor in
determining the oxidation state of copper. Strohmeier et al. takes a close look at the Cu Auger peaks to differentiate between CuAl₂O₄ and CuO.⁷¹

Figure 2.1: A. Surface of Fe metal before sputtering. B. Surface of Fe metal after sputtering for 5 min. Adapted from a figure in reference 72, with permission from ©IOP Publishing.

There are major drawbacks in studying the oxidation state of iron with the use of XPS. There is often an overlap in experimental data for the binding energies of Fe³⁺ and Fe²⁺. This can be seen in the NIST database, where there are reported binding energies of Fe²⁺ that range from 707.1 – 713.6 eV, and binding energies of Fe³⁺ that range from 708.3 to 711.6 eV.⁶⁸ This severe overlap makes it imperative to research the literature for materials with a chemical composition that is as close to the one being studied as possible.
Another major drawback is surface oxidation. The surface of Fe-containing materials is often easily oxidized when exposed to air. The surface oxidation in and of itself is not the problem, as most samples are sputtered with Ar ions to remove surface oxidation. The problem arises because the act of sputtering can reduce the iron. If the surface of a sheet of iron is not sputtered before the spectrum is obtained, then the spectrum will reveal only oxidized iron from the surface oxidation and not the elemental iron within the material, as can be seen in Figure 2.1A.\textsuperscript{72} When the same sample is sputtered for 5 min (Fig. 2.1B.), most but not all, of the surface oxidation is removed and the elemental iron is revealed. The sample needs to be sputtered enough to remove surface oxidation, yet care needs to be taken to not over sputter the sample so that the iron is reduced. Mills found that with as little as 1 min of sputtering, the iron in a sample

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure2.png}
\caption{A. Surface of Fe\textsubscript{3}O\textsubscript{4} before sputtering. B. 1 min. sputtering. C. 5 min. sputtering. D. 15 min. sputtering. E. 60 min. sputtering. Adapted from a figure in reference 72, with permission from ©IOP Publishing.}
\end{figure}
could be reduced (Fig. 2.2). This phenomenon is not unique to iron, but has also been observed in Ti and Ta. It is clearly evident in Figure 2.2 that 1 min of sputtering removed the surface oxidation because of the shift of the Fe 2p3/2 peak to a lower binding energy. The sample actually contains iron in both the 2+ and 3+ oxidation states. However, it is also evident in the spectra that the peak for elemental iron becomes apparent after 1 min of sputtering, and increases in intensity with increased sputtering time. Yamashita and Hayes developed a technique to reduce the effects of surface oxidation and reduction by sputtering. The difficult part of this study was that the samples were kept in an inert atmosphere until they were opened under vacuum in a chamber attached to the XPS instrument. This careful preparation removed the need for sputtering the surface oxidation from the sample, allowing for an accurate oxidation state determination of the standard samples. The resulting data from the standards were then used to precisely fit the peaks of samples of mixed oxidation states so that the ratio of Fe2+ and Fe3+ in each sample could be accurately determined. However, in this work, the ability to keep the samples in an inert atmosphere and prepare them for analysis was not possible with the instrumentation setup at hand.

Instrumental parameters can also play a role in the interpretation of experimental data. The two most common types of radiation used in XPS analysis are monochromatic Al Kα radiation, and monochromatic Mg Kα radiation. The choice, or availability, of radiation source can affect the spectrum that is produced as the peaks of certain elements may overlap with others, depending on the radiation source. One very important example would be the analysis of copper. Copper, when analyzed by Al Kα radiation produces auger peaks that can overlap with the 2p peaks of Mn or Fe. If at all possible, when
analyzing materials that contain copper and manganese or iron, a monochromatic Mg K\textsubscript{a} radiation source should be used so as to avoid an overlap of the peaks.

Another important parameter is the element used as a charge reference. The most commonly used reference is adventitious carbon, which is present in almost all samples. On the rare occasion when there is little to no adventitious carbon, whether due to sputtering or sample preparation, Ar 2p can be used as the charge reference as it is often present on all of the samples as an artifact of the Ar ion sputtering. The amount of oxidation present on the sample surface can be often be assessed by the intensity of the oxygen 1s peak. When surface oxidation is a concern, the sample may be further sputtered to reduce the oxidation. The O 1s peak is then used to indicate how much the sample may need to be sputtered. When choosing binding energy references, the oxidation state of the element should be taken into account, along with the chemical composition of the sample, and instrumental parameters. The conditions for the samples of the reference should be the same, or as closely matched to the experimental sample as possible.

XPS is employed in this work to determine, for the first time, the oxidation states of copper, indium, and sulfur in the CuIn\textsubscript{1-x}Fe\textsubscript{x}S\textsubscript{2} series. Assuming that the oxidation states are the intended oxidation states can contribute to a misinterpretation of the site occupancy of the elements, magnetic properties, as well as other physicochemical properties. Details of this work can be found in chapter 3.
2.3 $^{57}\text{Fe}$ Mössbauer Spectroscopy

$^{57}\text{Fe}$ Mössbauer spectroscopy can be used to determine the presence, oxidation state, local environment, and number of crystallographic unique locations of $^{57}\text{Fe}$ in the structure, as well as provide insight on magnetic properties. The sample is bombarded by $\gamma$-radiation, from a source that must be the same isotope as the iron in the sample so that the $\gamma$-rays will be of the correct energy to be absorbed by the sample. Iron Mössbauer spectroscopy utilizes a $^{57}\text{Co}$ source, which undergoes $\beta$-decay to $^{57}\text{Fe}$, which then emits $\gamma$-rays as it goes to the ground state.$^{77}$ The source is accelerated through a range of velocities which creates a Doppler Effect. Iron of a similar energy to the source will absorb the $\gamma$-rays and the detector measures the $\gamma$-radiation that passes through the sample; the spectra that are generated are plotted as velocity vs. intensity.

Three very important parameters to study in a Mössbauer spectrum are the isomer shift, quadropole splitting, and the magnetic splitting. The isomer shift is due to interactions between the nucleus and the electron density of the s-orbital within the nucleus. When there is a change in the electron density of the s-orbital that lies within the nucleus, this change will be demonstrated as a shift in the peak from zero, zero being determined by a known $\alpha$-$\text{Fe}$ metal standard. Bonding and oxidation state changes will exhibit themselves as an isomer shift. The quadropole splitting is exhibited in the form of a splitting of the tip of a single peak. This split can be small or large and is due to the interactions of the nuclear quadropole and the electric field gradient. The nuclear quadropole is a result of a non-spherical charge distribution.$^{78}$ The quadropole splitting is measured by the distance between the tips of the peaks that result from the split. The magnetic splitting, or hyperfine splitting as it is often called, can be seen as six peaks
within the spectra, and is due to the magnetic splitting of the nuclear energy levels in which there are only six possible transitions. Each crystallographically unique atom of study will have a unique Mössbauer peak within the spectrum. Thus, if there are two unique Fe ions within a material, there will be two peaks in the spectra, each one representing a different ion.

A great deal of Mössbauer studies focus on temperature dependent properties. Zhu et al. combined Rietveld refinement and Mössbauer spectroscopy in a magnetic temperature dependent study. Magnetic properties can also be studied at room temperature, as can be seen in Varnek’s research on iron doped CuCrS₂. There is an evolution of the magnetic sextet peaks, indicating an increase in ferromagnetic ordering, in relation to the increase in iron concentration. It is interesting to note that with as little as 2% Fe doping, the evolution of the magnetic peaks become apparent.

Johnston and Cardile’s study on natural minerals highlights the important trends in isomer shifts and quadropole splitting with respect to oxidation state and local environment. These findings are summarized in Table 2.1, with the last 4 listings representing iron in the 2+ oxidation state. The distinction between Fe²⁺ and Fe³⁺ can clearly be seen in the increase in the value of the isomer shift and of the quadropole splitting for Fe²⁺. The difference in the chemical environment of the iron is exhibited by less dramatic, but still significant changes in these values. Differentiation between both the I.S. and Q.S. for an octahedral and tetrahedral geometry is possible, as the tetrahedrally coordinated Fe³⁺ ions have both lower I.S and Q.S. values.
Table 2.1: Summary of Mössbauer spectroscopy analysis of various iron containing minerals from reference 81.

Drayton Montmorillonite = (Ca$_{0.27}$)(Si$_{3.49}$Al$_{0.51}$)(Fe$_{0.49}$Al$_{0.94}$Mg$_{0.82}$Ti$_{0.01}$),
Muloorinaillite = (Ca$_{0.059}$K$_{0.655}$)(Si$_{3.597}$Al$_{0.403}$)(Fe$_{0.628}$Al$_{0.969}$Mg$_{0.420}$),
Francosia Glauconite = (Ca$_{0.096}$K$_{0.725}$)(Si$_{3.611}$Al$_{0.389}$)(Fe$_{1.097}$Al$_{0.849}$Mg$_{0.442}$Ti$_{0.003}$Mn$_{0.001}$),
Fiji Glauconite = (Ca$_{0.076}$K$_{0.779}$)(Si$_{3.836}$Al$_{0.112}$Fe$_{0.051}$)(Fe$_{1.345}$Mg$_{0.595}$Mn$_{0.004}$)

<table>
<thead>
<tr>
<th>Mineral</th>
<th>I.S. (O$_h$) (mm/s)</th>
<th>Q.S. (O$_h$) (mm/s)</th>
<th>I.S. (O$_h$) (mm/s)</th>
<th>Q.S. (O$_h$) (mm/s)</th>
<th>I.S. (T$_d$) (mm/s)</th>
<th>Q.S. (T$_d$) (mm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Drayton Montmorillonite</td>
<td>0.37(1)</td>
<td>0.55(1)</td>
<td>-</td>
<td>-</td>
<td>0.10(2)</td>
<td></td>
</tr>
<tr>
<td>Muloorinaillite</td>
<td>0.36(1)</td>
<td>0.67(1)</td>
<td>0.37(1)</td>
<td>0.28(1)</td>
<td>-</td>
<td>0.26(2)</td>
</tr>
<tr>
<td>Francosia Glauconite</td>
<td>0.36(2)</td>
<td>0.63(2)</td>
<td>0.38(1)</td>
<td>0.28(1)</td>
<td>-</td>
<td>0.30(2)</td>
</tr>
<tr>
<td>Fiji Glauconite</td>
<td>0.44(1)</td>
<td>1.22(1)</td>
<td>0.35(1)</td>
<td>0.40(1)</td>
<td>0.25(1)</td>
<td>0.11(1)</td>
</tr>
<tr>
<td>Drayton Montmorillonite</td>
<td>1.29(3)</td>
<td>2.23(5)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Muloorinaillite</td>
<td>1.13(1)</td>
<td>2.85(1)</td>
<td>1.65(2)</td>
<td>1.18(3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Francosia Glauconite</td>
<td>1.24(2)</td>
<td>2.52(3)</td>
<td>1.46(1)</td>
<td>1.02(2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fiji Glauconite</td>
<td></td>
<td>1.28(1)</td>
<td>1.36(1)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^{57}$Fe Mössbauer spectroscopy is employed in this work in order to determine the oxidation state of Fe in Fe-substituted CuInS$_2$, as well as to explore the possibility of room temperature magnetic properties, such as ferromagnetism, ferrimagnetism, and antiferromagnetism. The oxidation state(s) of iron in this chalcopyrite structure should help to support the site occupancy of the ion within the crystal structure. An $^{57}$Fe Mössbauer study can also aid in the understanding of the magnetic behavior of the
materials under investigation. As we only had access to $^{57}$Fe Mössbauer measurements at room temperature, ferromagnetic or antiferromagnetic behavior at low or high temperatures could not be detected. Details of this study can be found in chapter 3.

2.4 Time of Flight Neutron Powder Diffraction

Neutron powder diffraction can be employed for structural analysis, such as phase identification and qualitative studies (such as the percent of each phase present in a compound), as well as be used to study magnetic fluctuation. The spallation neutron source (SNS) at Oakridge Nation Laboratory (ORNL) is equipped with a time of flight (TOF) neutron powder diffraction (NPD) instrument, POWGEN, BL-11A. SNS produces the most intense pulsed neutrons in the world.\textsuperscript{82}

Figure 2.3: Above left, the linear accelerator at the SNS, ORNL. Above right, the accumulator ring at the SNS, ORNL. Photos obtained from reference 82, with permission.
In this instrument set up, H\(^+\) ions are injected into the linear accelerator (LINAC) whereupon they pass through a foil that strips both electrons from the proton (Fig. 2.3).\(^{82}\) The resulting protons are passed into a ring in bursts, and are accumulated (Fig 2.3), after which they are released in a pulse and driven to hit a liquid mercury target (Fig 2.4).\(^{82}\) The force of the impact drives the neutron from the nuclei of the target. To reduce the energy so that it is usable for diffraction purposes, the neutrons pass through a moderator composed of decoupled poisoned supercritical H\(_2\).\(^{82}\) The neutrons are emitted in a spectrum of wavelengths and guided down the beamline to the instrument POWGEN. There is a series of choppers(rotating mechanical devices) that can be programmed to block all neutrons with the exception of those within the desired wavelength range. The time that it takes the neutrons to travel from the moderator to the detector is the time of flight.\(^{82}\) The range of wavelengths chosen for an experiment is reported using the center wavelength (CWL). Common wavelengths investigated are 1.066 Å CWL (0.4-2.8...
*d*-spacing) and 2.665 Å CWL (1.2-6.0 *d*-spacing). Typically, the data is reported as intensity (y-axis) versus *d*-spacing (x-axis).

![Diagram](image)

**Figure 2.5:** Penetration depth of neutron versus X-rays and electrons. Figure adapted from reference 83, with the permission of Roger Pynn.

Neutrons interact with the nuclear forces of an atom and, therefore, can penetrate deeper into the samples than X-rays or electrons (Fig. 2.5). The deeper penetration is due to the fact that one nucleus is 100,000 times smaller than the distance between two nuclei so the neutron, which is only a few Fermi’s in size (1 Fermi = 10^-15), can travel further into the sample before encountering a nucleus. This also makes neutron powder diffraction sensitive to magnetic scattering. It is possible to not only see the nuclear
structure of the materials being studied, but with certain materials the magnetic structure can also be discerned, which can differentiate, between ferromagnetic, ferromagnetic, and antiferromagnetic materials. Studies such as the evolution of the complex magnetic structure of hexagonal HoMnO$_3$ have employed neutron powder diffraction at various temperatures in order to better study the antiferromagnetic properties of the material.$^{84}$

Neutrons interact with the nucleus of an atom, and as each atom (as well as ions and isotopes) have varying neutron scattering factors, it is an excellent means to help discern the lattice parameters of a crystalline material as well as the site occupancy of the constituent atoms within the crystal structure. X-ray powder diffraction cannot easily distinguish between adjacent, or nearby, elements in the periodic table, nor can it distinguish between isotopes of the same element as the X-ray scattering factors are too similar because they are related to electron density therefore they follow a periodic trend. The use of NPD is quite advantageous as it can distinguish between atoms adjacent to each other on the periodic table, isotopes of the same element, and even light atoms that are often difficult to detect using X-rays.

The data from the neutron diffraction study is best understood when modeled using Rietveld refinement, a whole pattern fitting method using a least-squares analysis. Starting with an initial model, the refinement of that model describes the crystal structure of the material under study, including lattice parameters, fractional atomic coordinates, thermal displacement parameters, site occupancy, etc. The refinement of these parameters continues until the model matches as closely to the measured data as possible, while still making chemical sense. Details of the refinement methods are described in detail in chapters 3, 4, and 5. NPD was used in the current work to determine the phase purity and
refine the lattice parameters and site occupancy of Fe within the CuInS$_2$ I-42d crystal structure. The use of this characterization method contributed to the understanding of the anomalous behaviors of one of the solid solution members. These studies are in chapter 3 and 4 of this work.

2.5 Thermoelectric measurements

2.5.1 Sample Densification and Determination of Sample Density

Polycrystalline powdered materials need to be formed into a dense pellet for thermoelectric and conductivity measurements. It is important to produce a pellet as close to the theoretical density as possible or the subsequent measurements will not be indicative of the bulk polycrystalline material for example; a loosely packed powder may provide artificially low electrical conductivity measurements as the electricity will not flow through void spaces in the sample in the same way that it flows through a tightly packed powder. The relative density (referred to as bulk density in this work) is reported as a % or fraction of the theoretical density. Consolidation is carried out under dynamic vacuum, and consists of heating the sample from room to a temperature well below the melting point of the material, maintaining that temperature for a period of time, and slowly cooling back to room temperature. Typically, the temperature that is chosen is approximately 0.70 times the melting temperature (in Kelvin) of the material, which allows for sufficient mobility within the sample. Consolidation is concurrent with sample heating. The pressure increases with the temperature, and the sample is maintained at the
maximum pressure for a period of time before the pressure is slowly released. This method is important as it reduces the voids, providing grain to grain contact in the compact in order to improve the conductivity measurements. Caution must be taken not to heat the sample to a temperature that will induce phase changes. In a new material, in which the temperatures of the phase changes are unknown, it is advisable to first do a thermal analytical study to determine the temperature(s) of the phase change(s). Once the melting point and any other phase changes are determined, the maximum temperature can be determined as above, taking care not to exceed the temperature of any phase changes.

The density of the pre-dried, pressed samples can be determined by He-gas pycnometry. The instrument has two hollow chambers, with known volumes, separated by a valve. The chambers are purged of all atmospheric gases and sealed. The first chamber is pressurized to ~18 psig, while the second chamber, containing the sample, is allowed to equilibrate to atmospheric pressure (~0 psig). The valve is then opened, allowing the pressure to drop below that of the initial pressure in chamber one, and above that of the initial pressure in chamber two. The resulting pressure is noted, and the volume of the sample can be determined. The new volume of the chamber containing the sample (calculated using the ideal gas law) can be subtracted from the known value of the chamber to calculate the volume of the sample. The pressed samples need to be polished on both flat surfaces until the two sides are plane-parallel so that there is no variation in the width of the sample. The density of the pellet is then determined by the measurement of the pellet dimensions (volume) and the pellet mass. Errors of the geometrical density are made based on the uncertainties and errors of the constituent methods. In a solid solution, density as a function of composition can be investigated to see if it follows
Vegard’s Law. The density of the sample is needed for the thermal conductivity calculations as will be discussed in section 2.5.2. It is important to note any deviations from linearity in the density vs composition data as the density is used in the calculation of the thermal conductivity data. For example, if a sample has an unusually low pellet density (as compared to other compositions of the solid solution), then it would display an artificially low thermal conductivity value, owing to the inability of the phonons to travel unimpeded through the sample.

2.5.2 Thermal Conductivity

The thermal conductivity ($\kappa$) is a measurement of heat flow, along a linear path, through a sample due to a temperature gradient. Thermal conductivity determination can help to ascertain if a material under study has the potential not only for thermoelectric devices, but also for heat sinks or thermal insulators. Thermal conductivity ($\kappa$) values can be calculated using the equation $\kappa = \alpha C_p d$, where $\alpha$ is the thermal diffusivity, $C_p$ is the specific heat capacity, and $d$ is the bulk density of the sample (as determined from the geometric dimensions of the pellet and the mass of the pellet.). The lattice thermal conductivity ($\kappa_{\text{lattice}}$) of the samples is obtained by subtracting the electronic contribution (calculated using Wiedemann-Franz law, $\kappa_{\text{elec}} = \sigma L$) from the total thermal conductivity. $L$ is assumed to be $2.44 \times 10^{-8}$ W K$^{-2}$, which is the accepted value for degenerate semiconducting systems. The right cylinder densified pellets are coated with a thin layer of graphite and irradiated by a short laser burst, and the resulting rear face temperature rise is recorded and analyzed. Graphite is used as it eliminates any temperature anomalies during the measurements as it has high thermal conductivity along the face of the coating,
and it has very low thermal conductivity across the thickness of the coating. Pyroceram, a standard reference material used for thermal conductivity measurements because it has virtually zero thermal expansion and is stable up to 1200 K, was measured alongside each sample to facilitate the estimation of the sample’s heat capacity ($C_p$). The $C_p$ for the pyroceram standard is known, and when the thermal diffusivity ($\alpha$) is measured for the standard, the intensity of the flash ($\sigma$) is calculated with the equation, $\alpha = \sigma/dC_p$ (where $d$ is the depth of the material). The calculated value for $\sigma$, and the measured values of $\alpha$ and $d$ for the sample can be substituted into the same equation to solve for the $C_p$ of the sample.

The thermal conductivity is greatly affected by the structure of a crystalline solid. A well ordered crystal will allow phonons to travel unimpeded; as disorder and complexity are added to the crystal structure, the phonons are scattered and the thermal conductivity is decreased. As described in chapter 1, a decrease in thermal conductivity is an attractive prospect as it can enhance the ZT of a material. In this work, as structural complexity is being increased, a decrease in thermal conductivity is expected.

### 2.5.3 Thermopower and Electrical Conductivity

The thermopower, also known as the Seebeck coefficient, indicates the ability of a material to generate electricity when subjected to a temperature gradient. An in-depth description of a Seebeck device and its possible uses can be found in chapter 1. For these measurements, the samples need to be formed into rectangular bars, which are cut from the same pressed pellet that was used for the determination of the thermal conductivity,
using a precision wire saw. All of the samples need to be polished to a mirror-like finish and washed, so as to remove any contaminants and deviations in the surface.

The thermopower and electrical conductivity data for the samples are determined simultaneously. The sample is fixed between two nickel-based electrodes (current injections) with two voltage probes mechanically contacting the sample perpendicular to the flat and smoothly polished face of the sample. The determination of the thermopower is then performed under a residual pressure of He gas (~200 mbar) to facilitate a homogeneous distribution of heat inside of the furnace chamber. Heat is applied to the lower block of the sample, providing a temperature gradient. The Seebeck coefficient \( S \) is determined by the measurement of the temperature \( T \) on each end of the sample and the measurement of the current \( I \) from wires on the thermocouple that is placed on the end of the sample near the heat source, where \( S = -(\Delta V/\Delta T) \). The higher the absolute Seebeck coefficient, the higher the resulting voltage produced by the temperature gradient.

If the Seebeck coefficient is positive then the predominant carriers are holes, indicating that the material is \( p \)-type; if the Seebeck coefficient is negative, then the material is \( n \)-type. A predominantly \( p \)-type materials electrical field and temperature gradient will flow in the same direction while in a predominantly \( n \)-type material, they will flow in opposite directions. The charge carriers tend to move from the hot end to the cold end of the material, as can be seen in chapter 1, Figure 1.4. The determination of the Seebeck coefficient is very important to this work as it not only contributes to the determination of the ZT but also reveals the type of semiconductor which is very important in determining its placement in a photovoltaic device.
The electrical resistivity of a material measures how strongly the material resists the flow of electrons. Semiconductor materials, with relatively high electrical resistivity, may find use in circuit boards, while semiconducting materials that have low resistivity (high conductivity), may show promise as thermoelectric materials, if other qualifications have been met. The electrical resistivity is measured by a DC four-probe method. A constant current is applied to both ends of the sample and the voltage drop, between the wires of the same thermocouple, is measured. The resistivity ($\rho$) can easily be converted to electrical conductivity ($\sigma$) as $\rho = 1/\sigma$. The higher the electrical conductivity, the more advantageous it is to realizing a higher ZT for the material being studied. However it should be noted that the increases in the electrical conductivity of a material can often be accompanied by a loss in the Seebeck coefficient or an increase in thermal conductivity, making the optimization of ZT a very challenging proposition. In this work, with the transition element iron being the dopant, it is expected that the conductivity will increase with increasing amounts of iron.

There are a large number of potential applications for DLSs, as discussed in chapter 1, and many of their physicochemical characteristics are worthy of investigation. Reliance on only a few characterization methods cannot provide a complete picture of the materials structure and overall capabilities. Therefore, a number of analytical methods have been employed in this work, including those located at the more difficult to access National Laboratory facilities as well as instrumentation not commonly available to a chemist. The use of these techniques to reveal the structural and physicochemical characteristics of the DLSs investigated in this work are detailed in the following chapters.
2.6 References


77 http://serc.carleton.edu/research_education/geochemsheets/techniques/mossbauer.html [accessed 11-12-11]


83 Department of Energy, Oak Ridge National Laboratory,


3. Location and Oxidation State of Iron in Fe-substituted CuInS$_2$
Chalcopyrites$^{89}$

3.1 Introduction

Due to the flexibility of their composition, diamond-like semiconductors (DLSs) are an attractive class of compounds to investigate. DLSs have crystal structures that can be derived from either the cubic or hexagonal form of diamond.$^{90}$ ZnS, for example, crystallizes both in the sphalerite$^{91}$ structure type, which is a derivative of the cubic diamond structure, or the wurtzite$^{92}$ structure type, which is a derivative of the hexagonal diamond structure. The mental construct of cation cross-substitutions can lead to many ternary and quaternary diamond-like semiconductors.$^{93,94}$ CuInS$_2$ crystallizes in the chalcopyrite structure-type (I-42d)$^{95}$, and can be considered as an ordered superstructure of zinc blende where there are two sites for cations (Fig. 3.1). With copper occupying 4a and indium occupying 4b, the anion, sulfur, occupies the 8d site. A series of solid-solutions based on CuInS$_2$ can be created where the resulting physicochemical properties can be tuned and will depend on the composition and cation ordering of the materials.

DLS materials have a wide variety of potential applications from light emitting diodes,$^{96}$ spintronics,$^{97,98}$ nonlinear optics,$^{99}$ to solar cells, etc.$^{93}$ CuInS$_2$-based compounds are promising photovoltaic materials because they have high absorption coefficients of $\sim 10^{-5}$ cm$^{-1}$ and are direct band gap semiconductors, having a band gap ($\sim 1.5$ eV) that is close to optimal for use as the absorber layer in solar cells.$^{100,101}$ The research reported here is focused on substituting some of the expensive and ever depleting indium in CuInS$_2$ with iron, a much cheaper and more readily
available element. However, the majority of previous studies on doping CuInS₂ have focused on minimal amounts of substituents in order to elicit a property change.¹⁰⁹-¹¹⁶

With current photovoltaic devices employing $p$-type CuInS₂, it stands to reason that there have been several $ab$-$initio$ studies that focus on inducing the $p$-type conductivity of CuInS₂. As a result of these studies, it has been proposed that doping with Zn and Cd is projected to result in $p$-type materials, although the dopant concentration was unspecified.¹⁰¹ Doping of CuInS₂ with 4 atomic% or less of Zn has been proven to increase the band gap. Zn incorporation also

![Figure 3.1: Left: The structure of a zinc blende double unit cell as viewed down the crystallographic b-axis. (purple = zinc, yellow = sulfur) Right: The structure of CuInS₂⁹⁵, I-42d, as viewed down the crystallographic b-axis. (green = copper, red = indium, yellow = sulfur)](image)
increases the electrical conductivity, and 1 atomic % or less of Zn can also increase the open circuit voltage. Other experimental results indicate that N, P, As, Sb, and Bi are also good candidates, for not only creating p-type materials, but also increasing the conductivity of CuInS$_2$. Additionally Ge and Sn with atomic fractions as small as 2.5 x 10$^{-4}$, have been found to promote p-type conductivity.

The band gap of a member of a solid solution is known to lie somewhere between that of its two end members. The band gap of CuFeS$_2$ (0.60 eV$^{109}$), the mineral chalcopyrite$^{110}$, is significantly lower than the indium analog (1.53 eV$^{111}$). A theoretical study of Fe-doped CuInS$_2$, as well as experimental data, suggests that the resulting band gap will fall between 0.8-1.0 eV. $^{112,113}$ Tablero et al. undertook an ab initio study of CuIn$_{1-x}$Fe$_x$S$_2$, which proposed that Fe-substituted CuInS$_2$ should possess a relatively low band gap, that is reflective of an intermediate gap at 0.8 eV. $^{113}$ Interestingly, Luque et al. theorized that introducing deep energy levels, consisting of a large density of traps, within bulk alloys may provide for a more efficient solar cell than those cells produced with nanomaterials. $^{114}$ The phase diagram generated by Brun del Re et al. indicates that up to 20% Fe can be substituted for In while maintaining a phase-pure I-42d structure. $^{115,116}$ A more recent study of CuIn$_{1-x}$Fe$_x$S$_2$, using various synthetic routes, reports that a maximum of 10% Fe can be substituted while maintaining a phase-pure material. $^{117}$ However, in these experimental studies the site occupation of Fe and the oxidation states of the ions were not investigated.

Here we report, the synthesis of CuIn$_{1-x}$Fe$_x$S$_2$ via a simple high-temperature solid-state synthetic route. Previous work has shown a mixed site preference for a transition metal, Mn, substituted into a ternary chalcopyrite, CuInSe$_2$. $^{118}$ Therefore, the oxidation state and the site occupancy of the Fe in CuInS$_2$ is of great interest. The effects of the iron substitution on the
crystal structure and the oxidation state have been explored with the use of X-ray powder diffraction, neutron powder diffraction, Rietveld refinement, thermal analysis, optical diffuse reflectance spectroscopy, X-ray photoelectron spectroscopy (XPS), and Mössbauer spectroscopy.

3.2 Experimental

3.2.1 Reagents and Synthesis

All chemicals in this work were used as obtained: (1) copper: 100 mesh, 99.999%, Strem; (2) indium: 325 mesh, 99.99%, Strem; (3) iron: 22 mesh, 99.99%, Strem; (4) sulfur: sublimed, 99.5%, Fisher.

The CuIn$_{1-x}$Fe$_x$S$_2$ ($x = 0 - 0.30$) series of materials was prepared using high-temperature, solid-state synthesis. Stoichiometric amounts of copper, indium, and iron, with a slight excess of sulfur, were weighed in a glove box under argon. Each sample was prepared using 2 mmol of copper, a total of 2 mmol of iron and indium, and 4.4 mmol of sulfur. The sample was placed in a 9mm graphite tube which was inserted into a 12 mm od fused-silica tube. The graphite was used to prevent the iron from reacting with the fused-silica at high temperatures. The tube was then removed from the glove box and transferred to a vacuum line. The tube, under a vacuum of 10$^{-4}$ mbar, was flame sealed using a natural gas/oxygen torch. The sample was placed in computer-controlled furnace and the temperature was increased to 1150 °C over 24 hrs, held there for 72 hrs, and then decreased to 25 °C over a 24 hr period. The samples were removed from the fused-silica tubes, viewed under an optical microscope, and ground for characterization.
3.3 Physical Measurements

3.3.1 X-ray Powder Diffraction (XRPD) and Rietveld Refinement

X-ray powder diffraction data were collected using a PANalytical X’Pert Pro MPD powder X-ray diffractometer equipped with an X'Celerator detector, using copper K$_\alpha$ radiation with a wavelength of 1.54187 Å, a tube amperage of 40 mA, and a voltage of 45 kV. A 1/4° divergence slit, 1/2° anti-scatter slit, and a 0.02 rad soller slit at both diffracted and incident beams were set. The data were collected from 10 to 145 °2θ, with a step size of 0.008° and a scan speed of 0.010644 °/s. The samples were ground with an agate mortar and pestle for twenty minutes and a one hour scan was performed to confirm phase purity. The samples for refinement were then mixed with a high-purity silicon standard powder (NIST), and ground for 30 min before being loaded into a backfilled sample holder. The search and match capabilities of the X’Pert HighScore Plus program, along with the International Centre for Diffraction Data (ICDD) powder diffraction file (PDF) database, were employed in identifying crystalline phases. The X’Pert HighScore Plus program was used to determine the background of the full powder pattern and strip the K$_{\alpha2}$ peaks for easier evaluation of potential pattern matches. The program has a “search for peaks” option which determined the peaks present in the pattern however, it was necessary to visually assess the results and add peaks that were not designated as such by the program. Once the peaks were determined, the search and match function was utilized. This function combined the profile and peak data and matched it against patterns in the PDF database, after which it provided the most likely candidates for a phase match. The candidates that best matched the data where then chosen.
Rietveld refinements were performed with the use of GSAS and the EXPGUI interface.\textsuperscript{120,121} A Pseudo-Voigt function along with the Finger-Cox-Jephcoat asymmetry correction was used to model the peak profile. The background was refined using a shifted Chebyshev polynomial.\textsuperscript{122} Lattice parameters, background parameters, scale factor, sample displacement, peak shape parameters, atomic coordinates, isotropic displacement parameters, and indium and iron site occupation factors were refined. To determine an appropriate model; an attempt was made to refine Fe on the Cu site (4a) or to let all of the elements refine freely, the R factors increased and negative atomic displacement parameters for both Fe and Cu were a result so these models were rejected.

3.3.2 Optical Diffuse Reflectance UV/VIS/NIR Spectroscopy

Optical diffuse reflectance spectra were collected using a Cary 5000 UV/Vis/NIR spectrometer. BaSO\textsubscript{4} (Fisher, 99.92\%) was used as a 100\% reflectance standard. Solid samples were placed into a Harrick Praying Mantis\textsuperscript{TM} diffuse reflectance accessory that uses elliptical mirrors to focus the beam. Data were collected from 200 nm to 2500 nm. The wavelength was converted to energy and using the Kubelka-Munk equation, the percent reflectance data were converted absorption.\textsuperscript{123} Discontinuities in the plotted data resulting from detector changes during the scans were corrected by the addition of a correction factor to realign the data points. The absorption-energy curve was then used to estimate the band gap ($E_g$) by the extrapolation of the absorption edge to the baseline.
3.3.3 Inductively Coupled Plasma

Inductively coupled plasma optical emission spectrometry (ICP-OES) was performed by RJ Lee Group, Inc. (Monroeville, PA), operating in accordance with ISO 17025:2005 guidelines, as a means of quantitative analysis of the copper, indium, iron, and sulfur. Using high pressure XP1500 vessels in a MarsExpress CEM Microwave system, the samples were digested with trace metal nitric acid (Fisher Scientific). The samples were held at 180 °C for twenty minutes. A Varian 730ES ICP-OES was then utilized to analyze the digested samples for copper, indium, iron, and sulfur.

3.3.4 Differential Thermal Analysis

A Shimadzu DTA-50 thermal analyzer was employed to perform differential thermal analysis. The resulting data were recorded using the TA60-WS collection program. The instrument was calibrated using a 3-point calibration method, based on the melting points of indium, zinc, and gold metals. The instrument was calibrated to within an error of ±0.02 °C, as the data were reported in whole numbers; no error is reported for the phase transitions. For each experiment, the temperature was increased from 25 °C to 1100 °C at a rate of 10 °C/min and then decreased in ambient conditions until a temperature of 100 °C was achieved. A second cycle was performed to determine the reversibility of the events. Al₂O₃, obtained from Shimadzu Corporation, was used as the reference material. The reference and samples of comparable masses of ~0.2000 g, were sealed under a vacuum of ~10⁻⁴ mbar in carbon-coated, fused-silica ampoules. DTA residues were then examined by XRPD.
3.3.5 X-ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) was performed using a Thermo Scientific K-Alpha XPS instrument possessing monochromatized Al K$_\alpha$ radiation with a wavelength of 8.3386 Å (1486.7 eV), operating at 12 kV and 6 mA with an energy resolution of < 0.85 eV. The instrument uses a hemispherical electron energy analyzer equipped with a 128-channel detector system. Data were collected and processed using the Avantage software package from Thermo Scientific. Copper, silver, and gold calibration standards that are built into the sample stage were sputtered with 1000 eV argon ions to remove residual surface contamination and used to calibrate the energy scale via an automated instrument calibration routine that uses the Ag 3$d_{5/2}$, Au 4$f_{7/2}$, and Cu 2$p_{3/2}$ peaks. To prepare samples for analysis, the as-prepared ingots were covered with weigh paper and broken with a hammer. Pieces of the ingots that were relatively flat were then mounted onto a thin sheet of aluminum using vacuum-compatible, double-sided, carbon tape. Samples were sputtered with 1000 eV argon ions until the O 1$s$ peak from surface oxidation was no longer detected, or barely present. It is estimated that the samples were sputtered approximately 5000 Å relative to the sputtering rate of SiO$_2$. Ten scans were collected for survey spectra from -5.00 to 1350 eV binding energy. For all iron containing samples, high-resolution scans were preformed for the Cu 2$p$ and LM2 Auger, In 3$d$, Fe 3$p$ and 2$p$, S 2$p$, C 1$s$, O 1$s$, and Ar 2$p$ peaks. All of these scans, except those for Fe, were collected for CuInS$_2$. Fifteen scans for the Cu 2$p$, In 3$d$, and C 1$s$ peaks, twenty-five scans for the Cu LM2, S 2$p$ and O 1$s$ peaks, and fifty scans for the Fe 3$p$, Fe 2$p$, and Ar 2$p$ peaks were collected. Survey spectra and high-resolution spectra were obtained with an analyzer pass energy of 200 eV and 50 eV, respectively. The base pressure in the analysis chamber was typically 2 x 10$^{-9}$ mbar or lower. An
X-ray spot size of either 200 or 400 μm was used. All spectra were acquired with the charge neutralization flood gun turned on. The flood gun uses a combination of low energy electrons and argon ions. Spectra were charge corrected using the main Ar peak, $2p_{3/2}$ at 241.9 eV, due to Ar-ion-implantation in the sample after sputtering. In most cases sputtering removed all, or nearly all, adventitious carbon, which is usually used for charge correction. Reported binding energies were measured with a precision of ± 0.2 eV or better. Peak fitting was performed using mixed Gaussian/Lorentzian peak shapes and a Shirley-type background.

### 3.3.6 Mössbauer Spectroscopy

An MS-1200 constant acceleration spectrometer with a 10 mCi $^{57}$Co source diffused in a Rh matrix was used to collect room-temperature transmission Mössbauer spectra. The least-squares fittings of the Mössbauer spectra were performed with use of the NORMOS program (by RA Brand, distributed by Wissenschaftliche Elektronik GmbH, Germany). The instrument was calibrated with $\alpha$-Fe. However, the isomer shift is relative to the radiation source. The samples were prepared by grinding the ingots for twenty minutes into a fine powder.

### 3.3.7 Neutron Powder Diffraction (NPD) and Rietveld Refinements

Time-of-flight (TOF) neutron powder diffraction data for CuIn$_{0.85}$Fe$_{0.15}$S$_2$ were collected at the Spallation Neutron Source (SNS), Oak Ridge National Laboratory on the POWGEN powder diffractometer. POWGEN differs from nearly all other TOF neutron powder diffractometers due to a design that is based on combining diffracted neutrons collected at all angles into a single profile. This approach is used, rather than that of assigning the diffracted neutrons to a series of different profiles that traditionally were based on grouping detectors.
according to scattering angle. Such a unique approach gives rise to a high count rate while preserving excellent resolution ($\Delta d/d = 0.0015$ at a $d = 1 \text{ Å}$).\textsuperscript{125} The sample was ground into a fine powder and 1.6 g of the sample was loaded into a vanadium sample holder. Data were collected at room temperature using two different center wavelengths (CWLs) of 1.066 Å and 2.665 Å, which covered $d$-spacing ranges from 0.40 Å to 2.80 Å and from 1.20 Å to 6.0 Å. These energy bandwidths were ideally chosen in order to provide accurate information regarding the nuclear structure, and the site occupation factors as well as the atomic displacement parameters (ADPs).

Rietveld refinements were performed with the use of GSAS and the EXPGUI interface.\textsuperscript{120,121} The TOF peak profile function was used to model the data, and the background was refined using a shifted Chebyshev type.\textsuperscript{122} The crystallographic structure was refined using the CuInS$_2$ structure (I-42d)\textsuperscript{126}, as a starting model. Vanadium peaks, originating from the sample can, were evident; therefore, the vanadium structure (ICSD #171003) was added to the refinement. All refinements were performed to obtain accurate unit cell parameters, atomic coordinates, atomic displacement parameters, and site occupation factors. Background coefficients, scale factors, isotropic strain terms in the profile function and absorption were also refined for a total of 36 parameters. A model was employed, in which Cu, In, and Fe were allowed to refine on both the 4a and 4b sites. Negative occupancy values resulted for Cu(4a), In(4b), and Fe(4a), confirming that there was no antisite occupation and that the iron resided on the 4b site. When Fe was constrained to have the same atomic position and atomic displacement parameters as In, it resulted in an Fe(4b) occupation of 15.40% ($\chi^2 = 1.736$). Several other models were attempted with no satisfactory results.
3.4 Results and Discussion

3.4.1 Determination of Phase Purity

Thermal analysis of the unsubstituted sample, and the x = 0.15 iron sample, revealed similarities, as well as distinct differences between the two materials. The DTA thermograms (Fig. 3.2) revealed melting points of 1089 °C and 1088 °C for the unsubstituted and the x = 0.15 iron samples, respectively. These values were close to the reported melting point of 1090 °C for CuInS₂.\textsuperscript{127,128} Additionally two thermal events were observed that appear to be characteristic of the chalcopyrite-sphalerite and sphalerite-wurtzite phase transitions. The first phase transition for CuInS₂ was observed between 975-980 °C, and the second phase transition has been reported to occur at 1045-1050 °C.\textsuperscript{127,128} The phase transitions of the unsubstituted sample reasonably agreed with these reported values. The phase transitions in the x = 0.15 iron sample occurred at significantly lower temperatures (910 °C and 1013 °C, respectively). There were no additional phase transitions present with the incorporation of the iron. It was clearly observed that the substitution of iron for indium in CuInS₂ drives the phase changes to a lower temperature, suggesting that the iron is being successfully incorporated into the crystal structure. This same phenomenon was observed in Mn-substituted CuInSe₂ phases.\textsuperscript{118}
Figure 3.2: Differential thermal analysis thermograms for CuIn$_{1-x}$Fe$_x$S$_2$ where top: $x=0$ and bottom: $x=0.15$. The heating curves are in red and the cooling curves in blue, with peak temperatures reported for each transition. Exothermic events point upward, and endothermic events point down.

CuIn$_{1-x}$Fe$_x$S$_2$ samples were synthesized with $x$ varying between 0 and 0.30. A distinct secondary phase, CuIn$_5$S$_8$, was clearly present in the samples where $x \geq 0.20$.\textsuperscript{129} Rietveld
refinement helped to determine that this same secondary phase was also present in the $x = 0.175$ sample. Where $x \leq 0.15$, all samples appear to be phase pure and maintain the I-42d structure (Fig. 3.3).

![X-ray powder diffraction patterns](image)

**Figure 3.3:** X-ray powder diffraction patterns for CuIn$_{1-x}$Fe$_x$S$_2$, where $x = 0$ (JCPDS # 01-085-1575), 0.05, 0.075, 0.10, 0.125, and 0.15. The $(hkl)$ of the low intensity peaks were not labeled in order to improve clarity; all peaks can be indexed to the chalcopyrite structure.

ICP measurements of these samples were undertaken for quantitative analysis. The results indicate that the actual Fe/In ratio is in excellent agreement with the intended stoichiometry (Table 3.1). Samples of CuIn$_{1-x}$Fe$_x$S$_2$, where $x = 0.05$-$0.20$, were ground with an internal
silicon standard and analyzed using XRPD and subsequent Reitveld refinement. Samples where $x \leq 0.15$ refined with $R_p$ values under 5% and chi-squared values under two (Table 3.2, Fig. 3.4).

**Table 3.1:** Chemical composition of CuIn$_{1-x}$Fe$_x$S$_2$, where $x = 0.05$ - 0.15, measured by ICP. These formulae are normalized using the expected indium content.

<table>
<thead>
<tr>
<th>Intended Fe Content</th>
<th>Cu</th>
<th>In</th>
<th>Fe</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.065</td>
<td>1.000</td>
<td>0</td>
<td>2.011</td>
</tr>
<tr>
<td>0.075</td>
<td>1.044</td>
<td>0.925</td>
<td>0.073</td>
<td>1.980</td>
</tr>
<tr>
<td>0.100</td>
<td>1.004</td>
<td>0.900</td>
<td>0.106</td>
<td>1.949</td>
</tr>
<tr>
<td>0.125</td>
<td>1.003</td>
<td>0.875</td>
<td>0.128</td>
<td>1.942</td>
</tr>
<tr>
<td>0.150</td>
<td>1.034</td>
<td>0.850</td>
<td>0.160</td>
<td>2.031</td>
</tr>
</tbody>
</table>

**Table 3.2:** PXRD Rietveld refinement details for CuIn$_{1-x}$Fe$_x$S$_2$, where $x = 0.05$ - 0.20.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>$x=0.05$</th>
<th>$x=0.075$</th>
<th>$x=0.10$</th>
<th>$x=0.125$</th>
<th>$x=0.15$</th>
<th>$x=0.175$</th>
<th>$x=0.20$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Lattice</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Parameters</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a(Å)</td>
<td>5.51425(7)</td>
<td>5.51056(7)</td>
<td>5.50667(8)</td>
<td>5.50484(8)</td>
<td>5.50080(8)</td>
<td>5.50121(8)</td>
<td>5.50106(9)</td>
</tr>
<tr>
<td>c(Å)</td>
<td>11.1223(3)</td>
<td>11.1140(3)</td>
<td>11.1055(3)</td>
<td>11.0990(3)</td>
<td>11.0896(3)</td>
<td>11.0959(3)</td>
<td>11.0985(3)</td>
</tr>
<tr>
<td>Cell Volume(Å$^3$)</td>
<td>338.194(7)</td>
<td>337.486(7)</td>
<td>336.764(1)</td>
<td>336.341(1)</td>
<td>335.471(1)</td>
<td>335.799(9)</td>
<td>335.861(1)</td>
</tr>
<tr>
<td><strong>Cation 4a</strong> (Cu)</td>
<td>2.3(1)</td>
<td>2.94(7)</td>
<td>1.70(7)</td>
<td>1.33(7)</td>
<td>1.53(8)</td>
<td>2.42(8)</td>
<td>4.3(1)</td>
</tr>
<tr>
<td>$100U_{iso}(Å^2)$</td>
<td>1.43(6)</td>
<td>1.95(5)</td>
<td>1.95(5)</td>
<td>1.13(4)</td>
<td>1.63(5)</td>
<td>1.26(4)</td>
<td>2.47(5)</td>
</tr>
<tr>
<td><strong>Cation 4b</strong> (In/Fe)</td>
<td>0.229(1)</td>
<td>0.2360(6)</td>
<td>0.2293(6)</td>
<td>0.2254(6)</td>
<td>0.2234(6)</td>
<td>0.2223(7)</td>
<td>0.2292(9)</td>
</tr>
<tr>
<td>$100U_{iso}(Å^2)$</td>
<td>1.4(1)</td>
<td>1.83(7)</td>
<td>1.62(8)</td>
<td>1.41(8)</td>
<td>1.43(8)</td>
<td>2.07(9)</td>
<td>4.34(12)</td>
</tr>
<tr>
<td><strong>Anion 8d</strong> (S)</td>
<td>0.229(1)</td>
<td>0.2360(6)</td>
<td>0.2293(6)</td>
<td>0.2254(6)</td>
<td>0.2234(6)</td>
<td>0.2223(7)</td>
<td>0.2292(9)</td>
</tr>
<tr>
<td>$X_\text{c}$</td>
<td>1.875</td>
<td>1.715</td>
<td>1.992</td>
<td>1.989</td>
<td>1.983</td>
<td>2.155</td>
<td>3.122</td>
</tr>
<tr>
<td>$wR_p$</td>
<td>0.0555</td>
<td>0.0530</td>
<td>0.0566</td>
<td>0.0563</td>
<td>0.0550</td>
<td>0.0583</td>
<td>0.0690</td>
</tr>
<tr>
<td>$R_p$</td>
<td>0.0425</td>
<td>0.0402</td>
<td>0.0424</td>
<td>0.0424</td>
<td>0.0415</td>
<td>0.0425</td>
<td>0.0496</td>
</tr>
</tbody>
</table>
Figure 3.4: Difference plot generated by the Rietveld refinement of XRPD data from CuIn$_{0.875}$Fe$_{0.125}$S$_2$ (wR$_p$=0.0563, R$_p$=0.0424, $\chi^2$=1.989). Observed (+++ and calculated (solid line) X-ray powder diffraction patterns are on top. The difference is shown on the bottom. The 2 sets of tick marks indicate the expected Bragg reflections of the sample and the Si standard, from top to bottom respectively. The inset reflects the agreement between the observed and calculated data.

A linear decrease in the lattice parameters and cell volume was observed (Fig.3. 5). This trend follows Vegard’s Law$^{130}$, suggesting that the iron is randomly incorporated into the cation site(s) as one would expect to find in a true solid solution. A similar trend has also been observed when aluminum is substituted for indium in CuIn$_{1-x}$Al$_x$S$_2$; the lattice parameters decrease with each increasing Al substitution.$^{131}$ When $x \geq 0.175$ for CuIn$_{1-x}$Fe$_x$S$_2$ the linear decrease is no longer
present, and the cell volume remains essentially the same, suggesting that not all of the intended Fe incorporated into the chalcopyrite structure.

Figure 3.5: Top: Refined lattice parameters, a (triangle) and c (open circle), for CuIn$_{1-x}$Fe$_x$S$_2$, where $x = 0.05$-$0.20$, versus iron concentration. Bottom: Refined unit cell volume for CuIn$_{1-x}$Fe$_x$S$_2$, where $x = 0.05$-$0.20$, versus iron concentration. The lines are a linear fit to the data for $x = 0.05$ to 0.15, as those above this concentration break the trend. Note that the error bars are omitted as they were not distinguishable from the data point markers.
This differs from the study of Mn substituted CuInSe$_2$, where there was a linear increase in the lattice parameters with increasing Mn substitution. Even after a secondary phase became apparent there was still an increase in cell volume, though it was not necessarily linear.$^{118}$

Though the $R_p$ values remain the same for all samples ($x = 0.05 – 0.20$) of CuIn$_{1-x}$Fe$_x$S$_2$, the chi-squared values slightly increased as $x \geq 0.175$ and the difference plots revealed the presence of a secondary phase. When the site occupancy for indium and iron were refined, the percent of iron in the $x = 0.175$ and the $x = 0.20$ samples refined to $x = 0.160(2)$ and $x = 0.168(2)$ respectively. The current X-ray powder diffraction data, and subsequent Rietveld refinement suggests that Fe has successfully incorporated onto the In (4b) site in CuIn$_{1-x}$Fe$_x$S$_2$ ($x \leq 0.15$). However, one cannot assume that the Fe is in the 3+ oxidation state simply because it is residing on the In site. Nevertheless, the shrinking unit cell is evidence that the Fe is in the 3+ oxidation state because the incorporation of Fe$^{2+}$, with a larger radii than not only Fe$^{3+}$ but also In$^{3+}$ and Cu$^{2+}$ (0.77 Å, 0.63 Å, 0.76 Å, and 0.74 Å respectively)$^{132}$, would not result in this decrease of the unit cell.

**3.4.2 Oxidation State Determination**

The oxidation states of Cu, In, and S were determined through the use of XPS (Fig. 3.6). Even though the cracked ingot was loaded into the instrument within minutes, the surface of the
Figure 3.6: XPS spectra for CuInS$_2$(top) and CuIn$_{0.85}$Fe$_{0.15}$S$_2$(bottom) for Cu 2$p_{3/2}$, Cu 2$p_{1/2}$, In 3$d_{3/2}$, In 3$d_{5/2}$, S 2$p_{3/2}$, S 2$p_{1/2}$.

Table 3.3: XPS results for CuIn$_{1-x}$Fe$_x$S$_2$, where x = 0 - 0.15.

<table>
<thead>
<tr>
<th>x</th>
<th>Cu 2$p_{3/2}$ (eV)</th>
<th>In 3$d_{5/2}$ (eV)</th>
<th>S 2$p_{3/2}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>932.9</td>
<td>445.3</td>
<td>162.4</td>
</tr>
<tr>
<td>0.10</td>
<td>932.9</td>
<td>445.3</td>
<td>162.3</td>
</tr>
<tr>
<td>0.125</td>
<td>933.0</td>
<td>445.3</td>
<td>162.3</td>
</tr>
<tr>
<td>0.15</td>
<td>933.0</td>
<td>445.3</td>
<td>162.3</td>
</tr>
</tbody>
</table>

material was extensively oxidized, as evidenced by the amount of oxygen in the initial spectra. With enough sputtering, it was found that the surface oxidation could be completely or mostly removed depending on the sample. However, excessive sputtering resulted in a reduction of the
iron in the sample. Therefore, the oxidation state of iron in the samples could not be reliably determined by XPS.

Reduction of an element in a sample via sputtering is not uncommon with XPS analysis. The reduction of both Ti and Ta, due to Ar$^+$ ion sputtering has been reported. Suzuki et al. found that Fe$^{3+}$ is reduced to Fe$^{2+}$ in a matter of seconds in an iron oxide. Mills and Sullivan’s study of iron oxides revealed, not only the quick reduction of Fe$^{3+}$ to Fe$^{2+}$ by argon sputtering, but also of Fe$^{2+}$ to elemental Fe. A more reliable method to determine the oxidation state of iron in a sample was reported by Yamashita and Hayes, unfortunately the ability to crack the ingots under vacuum and load them directly into the spectrometer was not available in the current study. The binding energies for Cu, In, and S of the substituted samples ($x = 0.1, 0.125, 0.15$) were all within experimental error of the corresponding binding energies of the unsubstituted CuInS$_2$ (Table 3.3, Fig.3.6). The Cu $2p_{3/2}$ peak, at 932.9 eV, agreed well with previously published Cu$^{1+}$ values of 932.8 eV. The absence of a satellite peak in the region of 940 – 945 eV confirmed that Cu is not in the 2+ oxidation state. The presence or absence of this peak is an important indicator of the oxidation state of Cu as the range of binding energies of Cu$^{2+}$ $2p_{3/2}$ (932.7 - 934.1 eV) and those of Cu$^{1+}2p_{3/2}$ (932 - 932.8 eV) overlap. Cu$^{1+}$ and elemental copper can also have similar $2p_{3/2}$ binding energies. However, CuInS$_2$ is a well known I-III-VI$_2$ compound with copper in the 1+ oxidation state. Indium was found to be in the 3+ oxidation state with a binding energy of 445.3 eV for the In $3d_{5/2}$ peak, which is in reasonable agreement with the reported value of 445.6 eV, with the difference of 0.3 eV mostly likely due to a difference in instrument resolution or calibration procedures. The S $2p_{3/2}$ peak was also in good agreement with published values (161.6 - 162.9 eV) for S$^{2-}$ with a binding energy of 162.6 eV.
With the inability to accurately determine the oxidation state of iron with the use of XPS, Mössbauer spectroscopy was employed to do so. The substituted samples that were investigated (x = 0.10, 0.125, 0.15) showed no signs of magnetic hyperfine splitting at ambient temperatures (Fig. 3.7). These results were interesting as Fe-substituted CuCrS$_2$ starts to exhibit magnetic hyperfine splitting when x ≥ 0.05. However, Fe-substituted CuGaS$_2$ does not begin to exhibit magnetic behavior at room temperature until x ≥ 0.3. The Mössbauer spectra for each substituted sample in the present study was resolved by considering two quadrupole-splitting doublets, corresponding to two inequivalent sites for Fe in the respective structures. The combined values of the isomer shift and quadrupole splitting are indicative of the presence of Fe$^{3+}$ ions in the high-spin state (Table 3.4). These values are in reasonable agreement with previous studies of CuFeS$_2$ nanomaterials. The 1992 study of Brun del Re et al. of Fe-substituted CuInS$_2$ revealed the presence of both Fe$^{2+}$ and Fe$^{3+}$ in several samples, with isomer shifts at 0.6 mm/s and a quadrupole splitting of 2.2 mm/s for Fe$^{2+}$; these values are quite different for the Fe$^{3+}$ in these same samples (0.3 mm/s and 0.2 mm/s respectively).
Figure 3.7: Mössbauer spectra for a) CuIn$_{0.90}$Fe$_{0.10}$S$_2$, b) CuIn$_{0.875}$Fe$_{0.125}$S$_2$, and c) CuIn$_{0.85}$Fe$_{0.15}$S$_2$. The green and blue peaks indicate the separate peaks fitted to the data, while the red peak indicates the sum of these peaks.
Table 3.4: Mössbauer parameters for CuIn$_{1-x}$Fe$_x$S$_2$. I.S. - Isomer shift (relative to the source); Q.S. - Quadrupole splitting.

<table>
<thead>
<tr>
<th>x</th>
<th>I.S. (mm/s)</th>
<th>Q.S. (mm/s)</th>
<th>Abundance (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.398</td>
<td>0.185</td>
<td>47.29</td>
</tr>
<tr>
<td>0.100</td>
<td>0.090</td>
<td>0.544</td>
<td>52.71</td>
</tr>
<tr>
<td></td>
<td>0.392</td>
<td>0.052</td>
<td>68.15</td>
</tr>
<tr>
<td>0.125</td>
<td>0.104</td>
<td>0.725</td>
<td>31.85</td>
</tr>
<tr>
<td></td>
<td>0.508</td>
<td>0.045</td>
<td>94.12</td>
</tr>
<tr>
<td>0.150</td>
<td>0.185</td>
<td>0.339</td>
<td>5.88</td>
</tr>
<tr>
<td>Error</td>
<td>± 0.01</td>
<td>± 0.02</td>
<td>± 0.1</td>
</tr>
</tbody>
</table>

3.4.3 Verification of the Site Occupancy of Iron

The values obtained for the relative populations show that the preference of Fe for one of the inequivalent lattice sites increased with increasing iron content (Table 3.4). Considering the results of the Rietveld analysis it would be unlikely, though not impossible, for the Fe to occupy the Cu site as well as the In site. It is also unlikely that the Fe would be in the interstitial sites as it would most likely not be in the 3+ oxidation state, though a more in depth, temperature dependent study (such as those reported in references 155 and 156) would need to be undertaken in order to verify whether or not there is interstitial iron present. The Rietveld refinements would also have shown less iron on the In site when they were refined. There also would not likely be such a linear decrease in cell volume upon increasing amounts of Fe-substitution if the iron was not incorporating into the unit cell itself. It is more likely that the iron was not as randomly incorporated as suggested by Vegard’s Law with respect to the linear decrease in the cell parameters and the cell volume. There may be clustering of the Fe within the supercell.
There is a trend present in which the percent of the second Fe site decreased with increasing Fe substitution (Table 3.4). This may be a result of more long range ordering with increasing amounts of iron.

Figure 3.8: Difference plot generated by the Rietveld refinement of NPD data from CuIn$_{0.85}$Fe$_{0.15}$S$_2$ (wR$_p$ = 0.0192, R$_p$ = 0.0335, $\chi^2$ = 1.736). Observed (+++) and calculated (solid line) neutron diffraction patterns are on top. The difference is shown in the blue plot on the bottom. The 2 sets of tick marks indicate the Bragg reflections of the vanadium sample holder and the sample from top to bottom respectively.
The location of the iron within the crystal structure cannot be definitively determined from powder X-ray data alone due to the similar X-ray scattering factors of Cu and Fe. A neutron diffraction study of Mn-substituted CuInSe$_2$ found that the Mn, in the 2+ oxidation state, unexpectedly preferred the Cu site over the In site even under indium-poor synthetic conditions. Therefore to verify that Fe was only in the indium site, neutron powder diffraction, combined with Rietveld analysis, of CuIn$_{0.85}$Fe$_{0.15}$S$_2$ was employed. Neutron diffraction allows for the easy distinction between Cu and Fe because of the significantly different neutron scattering factors (8.03 fm and 11.62 fm, respectively). The neutron powder diffraction patterns had more background noise than typical due to the larger absorption cross section of indium (193.8 barn) and the length of the run (Fig. 3.8). The data, however, still allowed for an acceptable refinement of the site occupancy (Table 3.5).

Table 3.5: NPD Rietveld refinement details for CuIn$_{1-x}$Fe$_x$S$_2$, where x = 0.15.

<table>
<thead>
<tr>
<th>Lattice Parameters</th>
<th>Cation 4a (Cu1)</th>
<th>Cation 4b (In1/Fe1)</th>
<th>Anion 8d (S)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$(Å)</td>
<td>5.50336(6)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$c$(Å)</td>
<td>11.0994(2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cell Volume(Å$^3$)</td>
<td>336.167(8)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$100U_{iso}(Å^2)$</td>
<td>1.51(7)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$100U_{iso}(Å^2)$</td>
<td>2.1(2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$100U_{iso}(Å^2)$</td>
<td></td>
<td></td>
<td>1.20(7)</td>
</tr>
<tr>
<td>$X_s$</td>
<td></td>
<td></td>
<td>0.242(2)</td>
</tr>
<tr>
<td>$\chi^2$</td>
<td></td>
<td></td>
<td>1.736</td>
</tr>
<tr>
<td>$wR_p$</td>
<td></td>
<td></td>
<td>0.0192</td>
</tr>
<tr>
<td>$R_p$</td>
<td></td>
<td></td>
<td>0.0335</td>
</tr>
</tbody>
</table>

The Fe refined on the In 4b site, with a $\chi^2$ value of 1.736 and a $wR_p$ of 0.0192. This further confirms the refinement of the XRPD data that suggesting that the iron was occupying the indium site.
3.4.4 Band Gap Estimation

Optical diffuse reflectance measurements in the UV/Vis/NIR region were employed to estimate the band gap of the materials. Even with as little as 5% iron, the band gap decreased dramatically as compared to the unsubstituted CuInS\(_2\) (Fig. 3.9). The band gap ranges from 0.70 eV to 0.85 eV for all Fe-substituted samples, which is in good agreement with a previously reported value of 0.8 eV\(^{151}\). The band gaps lie much closer to that of CuFeS\(_2\) (0.60 eV\(^{109}\)) than that of CuInS\(_2\) (1.53 eV\(^{111}\)). This is most likely due to the introduction of an intermediate band consisting of delocalized \(d\) electrons. Tablero’s density of states study indicated that a band is formed that consists of the Fe \(d\) orbitals.\(^{113}\) A similar phenomenon was also observed in Teranishi’s study of CuAl\(_{1-x}\)Fe\(_x\)S\(_2\).\(^{152}\) It was observed, that with a minimal amount of

![Figure 3.9: Diffuse reflectance spectra for CuIn\(_{1-x}\)Fe\(_x\)S\(_2\) where, for clarity \(x = 0\), \(x = 0.05\), and \(x = 0.075\) are shown.](image)

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66
substitution, that an intermediate band was formed based on the hybridization of the Fe $d$ orbitals and the S $p$ orbitals.

3.5 Conclusion

Rietveld refinement of XRPD data for CuIn$_{1-x}$Fe$_x$S$_2$ ($x = 0.05 - 0.20$) indicates that up to 15% iron successfully substitutes for In in CuInS$_2$ and the materials maintain the chalcopyrite (I-42d) crystal structure. A secondary phase is observed when the iron substitution reached $x = 0.175$ and above. ICP data support the Rietveld refinement results, suggesting that the actual indium/iron stoichiometry is very close to the intended stoichiometry. The DTA thermograms indicate that the melting point remains virtually unchanged upon iron substitution, but the phase transitions shift to lower temperatures suggesting that the iron is being successfully incorporated into the crystal structure (up to $x \leq 0.15$). Refinement of both the XRPD and neutron diffraction data confirms that the iron resides in the indium (4b) site. The combination of XPS and Mössbauer spectroscopy reveals that the samples consist of Cu$^{1+}$, In$^{3+}$, Fe$^{3+}$, and S$^2$. The inequivalent Fe sites revealed by the Mössbauer spectroscopy suggest long range clustering that was not apparent in the neutron diffractograms because powder diffraction is in essence an averaging technique and the $x = 0.15$ sample included less than 6% of the second type of Fe.

While the synthesis of phase-pure CuIn$_{1-x}$Fe$_x$S$_2$ ($x = 0.05 - 0.15$) has been achieved, the estimated band gaps appear to decrease substantially with only a minimum amount of iron substitution. This band gap, however, may represent an intermediate band gap which could possibly be tuned through cosubstitution. Therefore the possibility of using iron to replace indium in the CuInS$_2$-based solar cells is still a viable idea, albeit with some further modifications.
3.6 References


Shay, J.L.; Wernick, J.H. *Ternary Chalcopyrite Semiconductors*; Pergamon, Oxford, **1973**.


XP Highscore Plus, PANalytical B.V., Almelo, the Netherlands.


4. Structure-Property Relationships Along the Fe-substituted CuInS$_2$ Series: Tuning of Thermoelectric and Magnetic Properties.\textsuperscript{153}

4.1 Introduction

Diamond-like semiconductors (DLSs) are of interest for applications in thermoelectrics,\textsuperscript{154,155} spintronics,\textsuperscript{156,157} photovoltaics,\textsuperscript{158} nonlinear optics\textsuperscript{159} and light emitting diodes.\textsuperscript{160} This wide variety of applications is due, in part, to the compositional flexibility of DLSs, which can be manipulated to tune the resulting physicochemical properties. The crystal structure of a DLS can be derived from either the cubic or hexagonal form of diamond, with half of the sites occupied by cations and the other half by anions.\textsuperscript{161} Further cation substitution, referred to as cross-substitution,\textsuperscript{158} of the binary DLSs can lead to ternary and quaternary compounds.\textsuperscript{162} CuInS$_2$ is a DLS that crystallizes in the I-42d space group (Fig. 4.1).\textsuperscript{163} This chalcopyrite structure can be considered an ordered superstructure of the cubic zinc blende structure, in which there are two cation sites. Copper occupies the 4a site and indium the 4b. The anion, sulfur, occupies the 8d site.
Figure 4.1: The crystal structure of CuInS$_2$ (I-42d), as viewed down the crystallographic $b$-axis.

Recently, several reports of promising thermoelectric properties for ternary and quaternary DLSs have attracted attention.$^{164-169}$ CuGaTe$_2$, CuInTe$_2$,$^{166}$ and Cu$_2$Sn$_{0.90}$In$_{0.10}$Se$_3$,$^{155}$ have promising ZT values of 1.4 at 950 K, 1.18 at 850 K and 1.14 at 850 K, suggesting that similar diamond-like materials may find applications in the conversion of waste heat into
electricity, provided that optimized ZT values necessary for the realization of practical devices can be obtained. The dimensionless figure of merit, ZT, is conventionally used to characterize the thermoelectric efficiency of a material. $ZT = \frac{\sigma S^2 T}{\kappa_{Tot}}$, where $\sigma$ is the electrical conductivity, $S$ is the Seebeck coefficient, $T$ is the absolute temperature, and $\kappa_{Tot}$ is the total thermal conductivity, comprised of both the electronic thermal conductivity ($\kappa_e$) and the lattice thermal conductivity ($\kappa_L$). Therefore, in order to improve existing thermoelectric candidates, the simultaneous increase in $\sigma$ and $S$, with a decrease in $\kappa$ is ideal, yet achievement of this is very challenging because the optimization of one of these properties is often at the expense of another. Toward this goal, it is critical to elucidate structure-property relationships in DLSs in order to better predict enhanced thermoelectric materials.

It has been suggested that the most promising approach to prepare enhanced thermoelectric materials is the creation of heavily-doped semiconductors with relatively narrow band gaps. In the case of CuInSe$_2$:Mn the introduction of 10% Mn results in an increase in ZT by over two orders of magnitude. Similarly, the introduction of 10% indium in the place of tin in Cu$_2$SnSe$_3$ results in an increase in ZT from 0.5 to 1.14 at 850 K. Likewise, quaternary DLSs such as Cu$_2$CdSnSe$_4$, Cu$_2$ZnSnSe$_4$, and Cu$_2$ZnSnS$_4$ have been doped with Cu and/or In in order to enhance their thermoelectric properties. Few of these studies provide detailed structural analysis of the DLSs; however, to truly advance this class of materials, a fundamental understanding of the structure-property relationships is necessary, for which high-quality structural studies are imperative.

In previous work, the iron in CuIn$_{0.85}$Fe$_{0.15}$S$_2$ was shown to reside on the 4b site, as evidenced by Rietveld refinement of neutron powder diffraction data. However, the background quality was poor due to the small sample size, short data collection time, and the
large absorption cross section of indium (193.8 barn). Toward the goal of structure-property correlations in these materials, a complete structural study of the entire CuIn$_{1-x}$Fe$_x$S$_2$ series, where $x = 0 - 0.15$, was undertaken using larger sample sizes and longer data collection times. Here we present the Rietveld refinement of both neutron and synchrotron X-ray powder diffraction data for the entire CuIn$_{1-x}$Fe$_x$S$_2$ series. These structural studies allow us to attribute structural features and secondary phase formation in the materials to the phenomena revealed by the thermoelectric and magnetic data presented here for the first time.

4.2 Experimental

4.2.1 Reagents

The chemicals in this work were used as obtained: (1) copper: 100 mesh, 99.999%, Strem Chemicals Inc. (Newburyport, MA, USA); (2) indium: 325 mesh, 99.99%, Strem Chemicals Inc. (Newburyport, MA, USA); (3) iron: 22 mesh, 99.99%, Strem Chemicals Inc. (Newburyport, MA, USA); (4) sulfur: sublimed powder, 99.5%, Fisher Scientific (Pittsburgh, PA, USA).

4.2.2 Synthesis

High-temperature, solid-state synthesis was employed to prepare the CuIn$_{1-x}$Fe$_x$S$_2$ ($x = 0 - 0.15$) series of materials, as described in previous work.$^{175}$

4.2.3 Neutron Powder Diffraction and Rietveld Refinement

Time-of-flight (TOF) neutron powder diffraction data for CuIn$_{1-x}$Fe$_x$S$_2$ ($x = 0 - 0.15$) were collected at the Spallation Neutron Source (SNS), Oak Ridge National Laboratory on the
POWGEN powder diffractometer. POWGEN is designed to combine diffracted neutrons collected from 30 to 150° 2θ into a single profile, which sets it apart from most other TOF diffractometers. This unique approach gives rise to a high count rate, while preserving the resolution ($\Delta d/d = 0.0015$ at a $d = 1 \AA$).

The 5 g samples were ground into fine powders and placed into 8mm vanadium cans. This is an increase of 3.4 g from the previous work on CuIn$_{0.85}$Fe$_{0.15}$S$_2$. Data were collected at two different center wavelengths (CWLs) of 1.066 Å and 2.665 Å, which covers $d$-spacing ranging from 0.40 to 2.80 Å and from 1.20 to 6.0 Å. The energy bandwidths were ideally chosen in order to provide accurate information regarding the nuclear structure and the site occupation factors, as well as the atomic displacement parameters (ADPs). All samples were collected at 300 K. Data for samples where $x = 0.125$ and 0.15 were also collected at 150 K, 75 K, and 15 K in order to explore the possibility of a magnetic structure.

Rietveld refinements were performed with the use of GSAS and the EXPGUI interface. For all samples, data from both CWLs (1.066 Å and 2.665 Å) were simultaneously refined, and the parameters and reliability factors for the combined refinements are reported (Table 1). The same model as previously reported for CuIn$_{0.85}$Fe$_{0.15}$S$_2$ was employed because satisfactory refinements could not be obtained with other choices of iron placement.

Data collected at 15 K, 75 K, 150 K, and 300 K for CuIn$_{0.875}$Fe$_{0.125}$S$_2$ and CuIn$_{0.85}$Fe$_{0.15}$S$_2$ were all refined; but only the data collected at the lowest temperature (15K) is reported in this work.

4.2.4 Synchrotron and Rietveld Refinement

Beamline 11-BM at the Advanced Photon Source (APS), Argonne National Laboratory was employed to collect high-resolution synchrotron powder diffraction data, using an average
wavelength of 0.413838 Å. Data were collected every 0.001 °2θ with a scan speed of 0.01 °/s using discrete detectors covering an angular range of -6 to 16 °2θ that were scanned over a 34 °2θ range, with a fixed energy of 30 KeV.

The X-ray optics on the 11-BM instrument consisted of two platinum-striped mirrors and a double-crystal Si(111) monochromator, with the second crystal having an adjustable sagittal bend.\textsuperscript{180} The incident flux was monitored by ion chambers. The analyzer system was comprised of twelve perfect Si(111) analyzers and twelve Oxford-Danfysik LaCl\textsubscript{3} scintillators, having a spacing of 2 °2θ, and positioned by a vertical Huber 480 goniometer equipped with a eidenhain encoder.\textsuperscript{181} The samples were spun during data collection. The samples were mounted on and dismounted from the diffractometer with a Mitsubishi robotic arm.\textsuperscript{180} All data were collected at room temperature.

The diffractometer was controlled via EPICS.\textsuperscript{182} Data were collected as the diffractometer was continuously rotated through 2θ. The instrument was calibrated using a mixture of NIST standard reference materials, consisting of Si (SRM 640c) and Al\textsubscript{2}O\textsubscript{3} (SRM 676). The Si lattice constant was used to determine the wavelength for each detector. Corrections were applied for 2θ offset, small differences in wavelength between detectors, detector sensitivity, and the source intensity, as noted by the ion chamber before merging the data into a single set of intensities evenly spaced in 2θ.

Rietveld refinements were performed as described above with a few exceptions; here the Pseudo-Voigt function along with the Finger-Cox-Jephcoat asymmetry correction was used to model the peak profile. The site occupation factors (SOFs) were not refined in these models. SOFs, were fixed to those refined from the neutron data, as neutron diffraction provides more
reliable SOFs in this case due to the greater disparity in neutron scattering factors of the constituent ions in comparison to their electron densities.\textsuperscript{176}

### 4.2.5 Sample Densification and Determination of Sample Density

The samples were hot pressed at 600 °C for 1 hr under an applied pressure of 100 MPa and cooled to room temperature over 2 hrs. The pellet densities were calculated using the pellet’s dimensions and mass, while the "true" powder density of each sample was measured by He-gas pycnometry on a Micromeritics Accupyc II 1340. The powder densities, pellet densities, and percent compaction as reported in Table 4.1. Additional details of the pressing procedure can be found in Chapter 2. It should be noted that because the different compacts, for the different compositions, all have different relative densities; the comparison of the thermal conductivity is less conclusive than if the compacts were of a similar relative density.

**Table 4.1:** Powder and pellet densities of CuIn\textsubscript{1-x}Fe\textsubscript{x}S\textsubscript{2} (x = 0 - 0.15). The standard deviations appear in parentheses.

<table>
<thead>
<tr>
<th></th>
<th>X = 0</th>
<th>X = 0.1</th>
<th>X = 0.125</th>
<th>X = 0.15</th>
</tr>
</thead>
<tbody>
<tr>
<td>Powder Density</td>
<td>4.899(6)</td>
<td>4.732(5)</td>
<td>4.797(3)</td>
<td>4.696(5)</td>
</tr>
<tr>
<td>(g/cm\textsuperscript{3})</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pellet Density</td>
<td>4.76(2)</td>
<td>4.32 (7)</td>
<td>4.70(1)</td>
<td>4.50(3)</td>
</tr>
<tr>
<td>(g/cm\textsuperscript{3})</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Percent Densification</td>
<td>97.1(4)</td>
<td>91.3(4)</td>
<td>98.0(3)</td>
<td>95.7 (6)</td>
</tr>
</tbody>
</table>

### 4.2.6 Thermal Conductivity

The thermal conductivity (κ) of each sample was determined as a function of temperature, from room temperature to 570K, using the flash diffusivity method on an LFA 457/2/G Microflash produced by Netzsch. The sample preparation details can be found in
chapter 2. Thermal conductivity (κ) values were calculated using the equation κ = αCₚd, where α is the thermal diffusivity, Cₚ is the specific heat, and d is the bulk density of the sample. A Pyroceram reference material was measured alongside each sample and Cₚ values for thermal conductivity calculations were derived from the laser flash data. Lattice thermal conductivity (κ_lattice) of the samples was obtained by subtracting the electronic contribution (calculated using the Wiedemann-Franz law, κₑₑₑ = σLT) from the total thermal conductivity. L was assumed to be 2.44 x10⁻⁸ WΩK⁻², the appropriate value for a degenerate semiconductor.

4.2.7 Thermopower and Electrical Conductivity

Thermopower and electrical conductivity data for the samples were measured simultaneously using a commercial ZEM-3 Seebeck coefficient/electrical resistivity measurement system produced by ULVAC-RIKO. Data were recorded in the temperature range of 300 K to 570 K. The electrical resistivity of the CuInS₂ and CuIn₀.₉Fe₀.₁S₂ samples could only be determined at elevated temperatures where the resistivities of the samples were within the measurable range of the instrument. Error bars for the electrical conductivity and subsequently calculated values for terms such as the power factor and ZT of CuInS₂ are artificially small, as this measurement was only able to be made once and therefore has no associated error. Additional details of sample preparation and measurements can be found in chapter 2.

4.2.8 Magnetic Measurements

Temperature- and field-dependent magnetic measurements of CuIn₁₋ₓFeₓS₂ (x = 0.0, 0.10, 0.125, 0.15) were carried out with a Quantum Design SQUID MPMS-5S magnetometer. The as-prepared powders of CuIn₁₋ₓFeₓS₂ were contained in gel capsule sample holders. The
magnetic susceptibility was corrected for the gel capsule and core diamagnetism with Pascal constants in each case. Measurements were taken from 2 K to 300 K in an applied field of $H = 0.01$ T. For the zero-field-cooled (ZFC) magnetization measurements, each sample was first cooled to 2 K in zero field, after which a magnetic field of 100 Oe was applied. The samples were then slowly warmed to 300 K for subsequent magnetization measurements. For the field-cooled (FC) magnetization measurements, the samples were cooled to 2 K with an applied field of 100 Oe and the susceptibility data were obtained upon heating. Isothermal field-dependent studies of the magnetization were conducted at 2 K using an external applied magnetic field ranging from -45 kOe to 45 kOe.

4.3 Results & Discussion

4.3.1 Neutron Powder Diffraction, Synchrotron Powder Diffraction, and Rietveld Refinement

Initial powder diffraction work of the CuIn$_{1-x}$Fe$_x$S$_2$ samples, prepared via high-temperature solid-state synthesis, indicated that the samples where $x = 0 - 0.15$ may be phase pure. However further studies were carried out using synchrotron X-ray powder diffraction as well as neutron powder diffraction using larger sample sizes and longer data collection times.

Using the neutron powder diffraction data, the models where $x = 0$, 0.1 and 0.125 refined with $\chi^2$ values well below 2, $wR_p$ values below 5% (Table 4.2) and had difference plots that were indicative of phase pure materials (Figure: 4.2, top).
Table 4.2: Rietveld refinement results for neutron(N) and synchrotron(S) data from CuIn$_{1-x}$Fe$_x$S$_2$, where $x = 0$-0.15.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>$x=0$ (N)</th>
<th>$x=0.1$ (N)</th>
<th>$x=0.125$ (N)</th>
<th>$x=0.15$ (N)</th>
<th>$x=0$ (S)</th>
<th>$x=0.10$ (S)</th>
<th>$x=0.125$ (S)</th>
<th>$x=0.15$ (S)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Cell</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$a$(Å)</td>
<td>5.52406(9)</td>
<td>5.5126(1)</td>
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<td>5.50093(3)</td>
<td>5.52005(6)</td>
<td>5.507721(8)</td>
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<td>11.1133(3)</td>
<td>11.0894(2)</td>
<td>11.0949(1)</td>
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<td>11.10329(3)</td>
<td>11.10122(3)</td>
<td>11.09667(3)</td>
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<td>337.718(1)</td>
<td>335.234(9)</td>
<td>335.734(4)</td>
<td>339.8241(8)</td>
<td>336.818(2)</td>
<td>336.536(1)</td>
<td>336.125(1)</td>
</tr>
<tr>
<td><strong>Cation 4a</strong></td>
<td></td>
<td></td>
<td></td>
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<td></td>
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</tr>
<tr>
<td>(Cu) SOF</td>
<td>0.97(1)</td>
<td>0.99(1)</td>
<td>1.00(1)</td>
<td>0.999(5)</td>
<td>1.00</td>
<td>0.99</td>
<td>1.00</td>
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<tr>
<td>100$U_{iso}$(Å$^2$)</td>
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<td>2.18(9)</td>
<td>0.50(4)</td>
<td>0.43(4)</td>
<td>1.66(2)</td>
<td>1.73(1)</td>
<td>2.02(1)</td>
<td>1.90(2)</td>
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<tr>
<td>(In/Fe) SOF</td>
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<td>0.931(0.13)</td>
<td>0.84(1)0.1224(0)</td>
<td>0.36(7)</td>
<td>1.00</td>
<td>0.90(1)</td>
<td>0.840.1224(0)</td>
<td>0.870.12</td>
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<td>100$U_{iso}$(Å$^2$)</td>
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<td>0.91(7)</td>
<td>0.21(5)</td>
<td>0.30(7)</td>
<td>1.376(8)</td>
<td>1.107(7)</td>
<td>1.047(6)</td>
<td>1.29(1)</td>
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<tr>
<td>(S) SOF</td>
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<td>1.00(1)</td>
<td>1.01(1)</td>
<td>0.967(8)</td>
<td>1.00</td>
<td>1.00</td>
<td>1.01</td>
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<td>0.33(4)</td>
<td>0.33(5)</td>
<td>1.02(2)</td>
<td>1.0092(2)</td>
<td>1.42(2)</td>
<td>1.39(2)</td>
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<tr>
<td>$X_s$</td>
<td>0.2260(6)</td>
<td>0.2275(7)</td>
<td>0.2280(6)</td>
<td>0.2275(7)</td>
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<td>0.2337(1)</td>
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<tr>
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<td>1.787</td>
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<td>1.833</td>
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<td>0.0477</td>
<td>0.0486</td>
<td>0.0593</td>
<td>0.1295</td>
<td>0.1139</td>
<td>0.1039</td>
<td>0.1406</td>
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The refined site occupation factors (SOFs) for $x = 0$, 0.1, and 0.125 agree very well with the intended stoichiometries. For the $x = 0.1$ sample, the SOF of iron on the 4b site, SOF(Fe)$_{4b}$, is 0.1021, while the $x = 0.125$ sample had a SOF(Fe)$_{4b}$ of 0.1224. There was a decrease in the unit cell volume and both lattice parameters ($a$ and $c$) as the amount of Fe-substitution increased in the samples from $x = 0$ to $x = 0.125$. This was expected, as the radius of four-coordinate Fe$^{3+}$ (0.63 Å) is smaller than that of four-coordinate In$^{3+}$(0.76 Å). As previously described, the low temperature measurements were performed in order to investigate possible magnetic ordering; however, no additional peaks were visible. It is possible that a canting of the spins could have potentially created a short-range magnetic ordering (small magnetic domains) observable by magnetic measurements, but not achievable per neutron diffraction except by the small contribution in the background.
Initial visual examination of the observed and calculated patterns for CuIn$_{0.85}$Fe$_{0.15}$S$_2$ at 75 K, 150 K, and 300 K gave no distinct evidence of a secondary phase. However, the Rietveld refinement of the data collected at 15 K revealed the presence of a few unindexed peaks of low intensity indicating a secondary phase (Fig. 4.2, bottom). The most intense of these peaks corresponds to 3.12 Å $d$-spacing, while two additional, smaller peaks were located at 1.91 and 1.63 Å $d$-spacing. The presence of this secondary phase was also evidenced in the reliability factors for the $x = 0.15$ refinement, where the $\chi^2$ is above three and the total wR$_p$ value is 0.0612. While these are not unreasonable values, they are noticeably higher than those of the other samples. Additionally, the SOF(Fe)$_{4b}$ refined to 0.1264 in this sample. As previously reported, ICP data confirmed the intended stoichiometry of this sample; therefore, in the case of the $x = 0.15$ sample, the remainder of the Fe is most likely in the secondary phase.$^{175}$
Figure 4.2: Neutron powder diffraction data difference plot for CuIn$_{1-x}$Fe$_x$S$_2$, Top: $x = 0.125$ and Bottom: $x = 0.15$, generated by Rietveld refinement. Observed (+++) and calculated (solid line) neutron diffraction patterns are on top in each plot. The difference is shown on the bottom. The tick marks indicate the expected Bragg reflections of the sample. The bottom inset shows the magnification of the largest unindexed peak for $x = 0.15$. 
Similar to the refinements using the neutron diffraction data, the synchrotron diffraction data collected for samples where \( x = 0.1 \) and \( x = 0.125 \) are indicative of phase-pure samples, as evidenced in the reliability factors and difference plots (Table 4.2, Fig 4.3, top). The \( x = 0.15 \) sample once again has a notably larger \( \chi^2 \) than that observed for the other samples, and a larger \( wR_p \) value of 0.1406. The difference plot reveals a very small, broad peak at \( \sim 12.4^\circ \) 2\( \theta \) (\( d \)-spacing = \( \sim 1.91 \) Å) (Fig. 4.3, bottom) that agrees with the low temperature neutron diffraction data. Additionally, there is a minima between two indexed peaks that does not fit well with the calculated pattern and the center of this area corresponds to a \( d \)-spacing of approximately 3.12 Å. There was no evidence of the peak at 1.63 Å, as in the case of the neutron diffraction pattern collected at 15 K.
Figure 4.3: Synchrotron powder diffraction data difference plot for CuIn$_{1-x}$Fe$_x$S$_2$. Top: $x = 0.125$ and Bottom: $x = 0.15$, generated by Rietveld refinement. Observed (+++) and calculated (solid line) synchrotron diffraction patterns are on top in each plot. The difference is shown on the bottom. The tick marks indicate the expected Bragg reflections of the sample. The bottom inset shows the magnification of the largest unindexed peak for $x = 0.15$. 
The insets found in Figs. 4.2(bottom) and 4.3(bottom) demonstrate the broad nature of the diffraction peaks of the secondary phase found in both the neutron (15 K) and synchrotron (RT) diffraction patterns of CuIn\textsubscript{0.85}Fe\textsubscript{0.15}S\textsubscript{2}. The three peaks at 3.12, 1.91 and 1.63 \AA\textit{d}-spacing are slightly shifted with respect to the major peaks of CuIn\textsubscript{5}S\textsubscript{8}, that occur at 3.08, 1.89 and 1.63 \AA\textit{d}-spacing. CuIn\textsubscript{5}S\textsubscript{8} was presumed to be the secondary phase in CuIn\textsubscript{0.8}Fe\textsubscript{0.2}S\textsubscript{2}, in our previous work\textsuperscript{185}.\textsuperscript{175} It still might be considered that Fe-substituted CuIn\textsubscript{5}S\textsubscript{8} is the secondary phase; however, Fe\textsuperscript{3+} substitution in CuIn\textsubscript{5}S\textsubscript{8} would decrease the unit cell parameters and correspondingly \textit{d}-spacing, not increase, as shown here. Additionally, while the two most intense peaks of the secondary phase corresponded well with the two most intense of CuIn\textsubscript{5}S\textsubscript{8}, the third and fourth most intense peaks were clearly not observed, 1.63 \AA\textit{d} being the fifth most intense peak. Interestingly, the three peaks in question do seem to fit well with a metastable cubic FeS;\textsuperscript{186} however, this is an unlikely candidate as it is metastable and contains Fe\textsuperscript{2+}, which is contraindicative with the previous Mössbauer spectroscopic measurements.\textsuperscript{175} Furthermore, the ICP data (Chapt 3) revealed all elements to be present in the intended stoichiometric amounts, so one would expect another minor phase along with the FeS to account for the Cu and In, and there is no evidence of such a phase.\textsuperscript{175} Another possibility, that is strongly preferred, is that the secondary phase is a cubic Fe-substituted CuInS\textsubscript{2}, as chalcopyrites are known to undergo phase transitions at high temperatures to sphalerite and wurtzite-type structures. This phenomenon was observed in the Ga-doped Cu\textsubscript{2}GeSe\textsubscript{3} system, in which a phase transition was induced by a Ga substitutional disorder.\textsuperscript{187} The transition to a cation disordered sphalerite-type phase is facilitated by the c/a ratio in these chalcopyrites that is nearly two, specifically 2.02 for the materials presented here.
In conclusion, in contrast to the previous reports of others and the conclusion drawn from laboratory X-ray powder diffraction data in this work, both neutron and synchrotron powder diffraction studies indicate that the solubility limit of iron in CuIn$_{1-x}$Fe$_x$S$_2$ is approximately $x = 0.125$. Although the secondary phase in the $x = 0.15$ sample is not definitively identified, it is believed to be a cubic iron-substituted CuInS$_2$ and its presence was important in the interpretation of the subsequent physicochemical property measurements.

4.3.2 Thermoelectric Properties

Fig. 4.4 shows the temperature dependence of the electrical conductivity for both the unsubstituted and the iron-substituted CuInS$_2$ samples. The resistivity of CuInS$_2$ was very high, precluding measurement at temperatures below 550 K. The electrical conductivity for CuInS$_2$ at 560 K was found to be $\sim 0.03$ S cm$^{-1}$. The electrical conductivity increased with increasing temperature for all samples, indicating typical semiconductor behavior.
Figure 4.4: Electrical conductivity of CuInS\(_2\) (▲), CuIn\(_{0.90}\)Fe\(_{0.10}\)S\(_2\) (●), CuIn\(_{0.875}\)Fe\(_{0.125}\)S\(_2\) (▼) and CuIn\(_{0.85}\)Fe\(_{0.15}\)S\(_2\) (■).

The electrical conductivity also increases with increasing iron-content, with a significant increase for the 12.5% and 15% samples, to 0.19 Scm\(^{-1}\) and 0.39 Scm\(^{-1}\), respectively at 560 K. An increase in conductivity in Mn-substituted CuInSe\(_2\) was also observed, with the greatest increase being from 0.09 Scm\(^{-1}\) in the unsubstituted sample to 2.9 Scm\(^{-1}\) in CuIn\(_{0.95}\)Mn\(_{0.05}\)Se\(_2\) at 560 K. However, with greater Mn substitution, the conductivity began to decrease.\(^{172}\) The increase in the electrical conductivity in these materials has been explained as the generation of more conducting pathways in the diamond-like materials. Extrapolation of this concept to
CuInS$_2$ would suggest that the Cu and S are bonded to form the electrically conducting unit (ECU) in these materials and the In-S network is considered as the electrically insulating unit (EIU).\textsuperscript{173} Insertion of iron in place of indium, therefore, breaks up this electrically insulating unit and creates more avenues for the carriers. For instance, although the isoelectronic substitution between In$^{3+}$ and Fe$^{3+}$ is not expected to increase the intrinsic density of free-carriers in CuIn$_{1-x}$Fe$_x$S$_2$ samples, a reduction of the band gap energy is possible. With increasing Fe-substitution, the activation energy was found to decrease, from 0.35 eV for the $x = 0.10$ sample, to 0.34 eV for the $x = 0.125$ sample, with the lowest activation energy being 0.24 eV for the $x = 0.15$ sample. This implies that thermally activated carriers (arising from thermal excitation of electrons from the valence band to the conduction band) contribute to the electrical conduction (intrinsic semiconducting regime) at lower temperatures. Therefore, a reduction in the band gap of CuIn$_{1-x}$Fe$_x$S$_2$ samples with increasing Fe content should result in an increase in the carrier density at a given temperature. This explanation is consistent with the observed increase in the electrical conductivity with increasing $x$ values at a constant temperature.

The Seebeck coefficient was measured as a function of temperature for the CuIn$_{1-x}$Fe$_x$S$_2$ samples (Fig. 5). The Seebeck coefficient was positive at all temperatures for the unsubstituted sample, indicating holes as the dominant charge carriers ($p$-type). Conversely all iron-substituted samples are $n$-type as exhibited by the negative Seebeck coefficient at all temperatures measured. The Seebeck coefficient for CuInS$_2$ is 44 $\mu$VK$^{-1}$ at room temperature and it increases to 149 $\mu$VK$^{-1}$ at 560 K. These values are smaller than those obtained for the corresponding selenide, CuInSe$_2$, which has a Seebeck coefficient of -206 $\mu$VK$^{-1}$ at 560 K.\textsuperscript{172} Interestingly, the Seebeck coefficient increases with increasing temperature for both the $x = 0$ and $x = 0.125$ samples, while
there is very little temperature dependence observed for the $x = 0.10$ and $x = 0.15$ samples. CuIn$_{0.875}$Fe$_{0.125}$S$_2$ sample exhibits the largest thermopower with values of approximately -275 $\mu$VK$^{-1}$ at room temperature and -172 $\mu$VK$^{-1}$ at 560 K, a vast improvement over the unsubstituted CuInS$_2$. The observed change in the majority carrier type from holes to electrons again suggests that the insertion of Fe$^{3+}$ at the In$^{3+}$ site in the structure of CuInS$_2$ drastically alters the electronic band structure of the resulting CuIn$_{1-x}$Fe$_x$S$_2$ samples near the Fermi level. Therefore, a change in the carrier effective mass ($m^*$) in various CuIn$_{1-x}$Fe$_x$S$_2$ compositions is

![Figure 4.5: Temperature dependence of Seebeck coefficient for CuInS$_2$ (▲), CuIn$_{0.90}$Fe$_{0.10}$S$_2$ (●), CuIn$_{0.875}$Fe$_{0.125}$S$_2$ (▼) and CuIn$_{0.85}$Fe$_{0.15}$S$_2$ (■).]
also anticipated. This explains the large variations in the thermopower of the CuIn1-xFxS2 samples.

Fig. 4.6 displays the temperature dependence of the total thermal conductivity, while the inset depicts the thermal behavior of the lattice contribution, \( \kappa_L \). The \( \kappa_{\text{Tot}} \) for CuInS2 was measured as 5.71 Wm\(^{-1}\)K\(^{-1}\) at room temperature and this decreased to 2.05 Wm\(^{-1}\)K\(^{-1}\) at 540 K. Iron substitution in this system resulted in a significant reduction of the \( \kappa_{\text{Tot}} \). CuIn\(_{0.875}\)Fe\(_{0.125}\)S\(_2\) has a \( \kappa_{\text{Tot}} \) of 2.95 and 1.37 Wm\(^{-1}\)K\(^{-1}\) at room temperature and 540 K, respectively. The rapid decrease in thermal conductivity as a function of temperature indicates that the thermal transport is dominated by acoustic phonon scattering.\(^{188}\) The \( \kappa_{\text{Tot}} \) values for these iron-substituted CuInS\(_2\) materials are competitive with some of the best diamond-like materials to date, for example Cu\(_{2.10}\)Zn\(_{0.90}\)SnSe\(_4\), which has a \( \kappa_{\text{Tot}} \) of 1.28 Wm\(^{-1}\)K\(^{-1}\) and a ZT of 0.91 at 860 K.\(^{174}\)

A low \( \kappa_{\text{Tot}} \) is often found for materials with complex crystal structures of low symmetry, comprised of relatively heavy atoms.\(^{170}\) The chalcopyrites in this work are composed of relatively lighter atoms, and crystallize in a body-centered tetragonal crystal structure. It is believed that the decrease in \( \kappa_{\text{Tot}} \) is due to phonon scattering from the effect of mass fluctuation, assuming that the samples represent members of a solid solution series. The doping is also believed to increase lattice distortion further from the perfect diamond structure owing to the ordering of the varying sized cations, thus resulting in a lower \( \kappa_{\text{Tot}} \). Additionally, chalcopyrite-type systems inherently possess low thermal conductivity values even at room temperature and with no doping. This is due to the large number of possible defects typically observed in these materials; for example antisite occupation, such as indium on a copper site, In\(_{\text{Cu}}\), or copper on an indium site, Cu\(_{\text{In}}\), as well as vacancies on either the copper or sulfur sites, \( V_{\text{Cu}} \) and \( V_{\text{S}} \) respectively.\(^{189, 190, 191}\)
The thermal conductivity of CuIn_{0.85}Fe_{0.15}S_{2} is unexpectedly high (Fig. 4.6). However, this sample, based on solid solution behavior, is expected to display the lowest thermal conductivity of all of the samples measured. Instead, CuIn_{0.85}Fe_{0.15}S_{2} displays a thermal conductivity greater than every sample except CuInS_{2} at elevated temperatures. The anomalous behavior of the x = 0.15 sample can most likely be attributed to the presence of the secondary phase.

Figure 4.6: Thermal conductivity and lattice thermal conductivity (inset) as a function of temperature for CuInS_{2} (▲), CuIn_{0.90}Fe_{0.10}S_{2} (●), CuIn_{0.875}Fe_{0.125}S_{2} (▼) and CuIn_{0.85}Fe_{0.15}S_{2} (■).
It is interesting to note that $\kappa_{\text{Tot}}$ decreases commensurate with increasing Fe incorporation, until the limit of phase purity. A continuous decrease in $\kappa_{\text{Tot}}$ along a solid-solution series is not always observed for the diamond-like materials. In the case of Cu$_2$Mn$_x$Sn$_{1-x}$Se$_3$ there is an optimal value of $x = 0.01$. When doping exceeds this amount the thermal conductivity begins to increase for $x = 0.02$ and $x = 0.05$. Likewise the Seebeck coefficient is also larger for the 0.01 sample.\textsuperscript{192} Additionally in the Cu$_2$Ga$_x$Ge$_{1-x}$Se$_3$ system, it is the undoped sample that actually displays the lowest $\kappa_{\text{Tot}}$.\textsuperscript{187} It is believed that these differences are due to the highly complex nature of diamond-like structure defects that are often dependent upon dopant choice, dopant concentration and preparation method, among other variables.
Table 4.3: Thermoelectric properties of select diamond-like semiconductors. T = temperature, σ = electrical conductivity, S = Seebeck coefficient, κ = thermal conductivity, ZT = dimensionless figure of merit for thermoelectric

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<th>Compound</th>
<th>T (K)</th>
<th>σ (Scm⁻¹)</th>
<th>S(μVK⁻¹)</th>
<th>κ(Wm⁻¹K⁻¹)</th>
<th>ZT</th>
<th>Ref.</th>
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<td>156</td>
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<td>2.2 x 10⁻⁴</td>
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<td>~283</td>
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<td>166</td>
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<td>CuInTe₂ (annealed 7 days)</td>
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<td>0.14</td>
<td>~283</td>
<td>~1.0</td>
<td>1.18</td>
<td>166</td>
</tr>
<tr>
<td>Cuₙ₀₄InTe₂</td>
<td>702</td>
<td>~14.2</td>
<td>~310</td>
<td>~0.54</td>
<td>0.17</td>
<td>193</td>
</tr>
<tr>
<td>CuGaTe₂</td>
<td>950</td>
<td>227</td>
<td>244</td>
<td>~0.89</td>
<td>1.4</td>
<td>164</td>
</tr>
<tr>
<td>Cuₙ₋₁GaSb₃Te₂</td>
<td>721</td>
<td>~156</td>
<td>~262</td>
<td>~0.72</td>
<td>1.07</td>
<td>165</td>
</tr>
<tr>
<td>(ₙ=0.02)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu₉₈Sb₉₇₅Sn₀₂Se₄</td>
<td>673</td>
<td>~229</td>
<td>~238</td>
<td>~1.16</td>
<td>0.75</td>
<td>194</td>
</tr>
<tr>
<td>AgInSe₂</td>
<td>724</td>
<td>~7.6</td>
<td>~470</td>
<td>~0.35</td>
<td>0.34</td>
<td>168</td>
</tr>
<tr>
<td>Cu₂Mn₀₁Sn₉₉Se₃</td>
<td>715</td>
<td>~695</td>
<td>~114</td>
<td>~1.59</td>
<td>0.41</td>
<td>192</td>
</tr>
<tr>
<td>Cu₂Mn₀₂Sn₉₈Se₃</td>
<td>715</td>
<td>~726</td>
<td>~111</td>
<td>~1.89</td>
<td>0.34</td>
<td>192</td>
</tr>
<tr>
<td>Cu₂Mn₀₅Sn₉₅Se₃</td>
<td>715</td>
<td>~1161</td>
<td>~83.1</td>
<td>~2.12</td>
<td>0.27</td>
<td>192</td>
</tr>
<tr>
<td>Cu₉₉Ge₉₃Se₃</td>
<td>745</td>
<td>~11.78</td>
<td>446</td>
<td>0.67</td>
<td>0.28</td>
<td>187</td>
</tr>
<tr>
<td>Cu₂Ga₀.₇₀Ge₀.₉₃Se₃</td>
<td>745</td>
<td>~368</td>
<td>~150</td>
<td>~1.38</td>
<td>0.50</td>
<td>187</td>
</tr>
</tbody>
</table>

Iron substitution in CuInS₂ results in an increase in the ZT for all materials with the exception of the x = 0.10 sample (Table 4.3, Figure 4.7). The highest ZT for the Fe-substituted
samples is \(2.2 \times 10^{-4}\) at 560 K for CuIn\(_{0.875}\)Fe\(_{0.125}\)S\(_2\), an increase of over an order of magnitude from the unsubstituted sample with a ZT value of \(1.71 \times 10^{-5}\). The \(x = 0.15\) sample is once again anomalous; this can be best explained by the presence of a secondary phase in the \(x = 0.15\) sample that is not present in the other samples. This behavior is similar to the Cu\(_2\)Mn\(_x\)Sn\(_{1-x}\)Se\(_3\) series, where the addition of manganese beyond the solubility limit results in a negative effect on the thermoelectric properties of Cu\(_2\)Mn\(_x\)Sn\(_{1-x}\)Se\(_3\).\(^{192}\)

![Figure 4.7: The thermoelectric figure of merit, ZT, as a function of temperature for CuInS\(_2\) (▲), CuIn\(_{0.90}\)Fe\(_{0.10}\)S\(_2\) (●), CuIn\(_{0.875}\)Fe\(_{0.125}\)S\(_2\) (▼) and CuIn\(_{0.85}\)Fe\(_{0.15}\)S\(_2\) (■).](image)

While an improvement in all thermoelectric parameters (increase in \(\sigma\), increase in \(S\) and decrease in \(\kappa_{\text{Tot}}\)) have been observed upon doping, this is not the case for other DLSs. In the case
of Cu$_{2+x}$Cd$_{1-x}$SnSe$_4$, the highest ZT, 0.65, was attained for the most highly doped sample, Cu$_{2.10}$Cd$_{0.90}$SnSe$_4$. In this system the electrical conductivity increases with increasing copper content, tripling in value for the Cu$_{2.10}$Cd$_{0.90}$SnSe$_4$ sample, while the thermal conductivity decreases; however, the thermopower decreases from 204 to 156 $\mu$V/K for $x = 0$ to $x = 0.10$ respectively.\textsuperscript{173} In the Cu$_{2+x}$Zn$_{1-x}$SnS$_4$ system, an increase in copper from $x = 0$ to $x = 0.10$ resulted in a 25-fold enhancement of the electrical conductivity and a decrease in $\kappa_{\text{Tot}}$; however, these gains are accompanied by an even greater loss in the thermopower, from 355 to 211 $\mu$V/K.\textsuperscript{174} Similar results were observed for Cu$_2$ZnSnSe$_4$ system doped with copper. Interestingly, substitution of indium for tin in Cu$_2$ZnSnSe$_4$ resulted in less of an increase in the electrical conductivity accompanied by an even greater loss in thermopower along with an undesirable increase in the thermal conductivity.\textsuperscript{174} It has been demonstrated that transition metal doping in both CuInS$_2$ and CuInSe$_2$ results in simultaneous improvement of all thermoelectric parameters using the Fe-substituted CuInS$_2$ samples presented here, as well as the previously reported Mn-substituted CuInSe$_2$ samples.\textsuperscript{172} To the best of our knowledge, these are the only heavily-doped/substituted diamond-like systems thus far that have been shown to behave in this way.

4.3.3 Magnetic Properties

The temperature dependence of the magnetization for CuInS$_2$ under zero field cooled (ZFC) and field cooled (FC) conditions was measured with an applied field of 100 Oe. There is no difference between the ZFC and FC data for this material. The compound exhibits typical paramagnetic behavior with a low susceptibility.
The magnetic susceptibility versus temperature data for both CuIn$_{0.95}$Fe$_{0.05}$S$_2$ and CuIn$_{0.9}$Fe$_{0.1}$S$_2$ indicate that the samples are typical paramagnets (Fig. 4.8).

![Graph showing temperature dependence of magnetic susceptibility](image)

Figure 4.8: Temperature dependence of magnetic susceptibility of CuIn$_{0.9}$Fe$_{0.1}$S$_2$ at 100 Oe under ZTC conditions. The inset shows the temperature dependence of the magnetic susceptibility measured under ZFC and FC conditions at an applied field of 100 Oe.

The inverse magnetic susceptibility as a function of temperature displays typical Curie-Weiss behavior over the temperature range of 140-300 K for $x = 0.05$ and 220-300 K for $x = 0.10$. These paramagnetic data were fitted to the Curie-Weiss equation, $1/\chi = 1/C[(T - \theta)$, where $C$ is the Curie constant, and $\theta$ is the Weiss temperature. This resulted in Curie constants (4.43(3) and 3.68(3) emu·K·mol$^{-1}$, respectively) and Weiss temperatures (-141(2) and -213(3) K, respectively) that are indicative of weak antiferromagnetic ordering in these materials. The calculated $\mu_{\text{eff}}$, 5.95(5), for the $x = 0.05$ sample agreed with the ideal value of 5.92 $\mu_B$ for a
spin-only value of $d^5\text{Fe}^{3+}$. The $x=0.10$ sample had a calculated $\mu_{\text{eff}}$ of 5.4(5) $\mu_B$, which was only slightly lower than the expected value (Table 4). These findings were consistent with the field dependence data reported by Tsujii for CuIn$_{0.90}$Fe$_{0.10}$S$_2$.\textsuperscript{196} A study undertaken by Brun del Re agreed with the negative Weiss temperature reported here for the $x=0.10$ sample; however, the value in that report is much smaller and the samples contained some amount of Fe$^{2+}$ that varied depending upon the synthetic conditions employed as indicated by Mössbauer spectroscopy.\textsuperscript{197}
Figure 4.9: Top: Temperature dependence of magnetic susceptibility of CuIn$_{0.875}$Fe$_{0.125}$S$_2$ at 100 Oe under ZFC conditions. The insets shows the temperature dependence of the magnetic susceptibility measured under ZFC and FC conditions at an applied field of 100 Oe. Bottom: Temperature dependence of magnetic susceptibility of CuIn$_{0.85}$Fe$_{0.15}$S$_2$ at 100 Oe. The insets show the temperature dependence of the magnetic susceptibility measured under ZFC and FC conditions at an applied field of 100 Oe.
The temperature dependence of the magnetic susceptibility for CuIn$_{0.875}$Fe$_{0.125}$S$_2$, in an applied field of 100 Oe, is shown in Fig. 4.9 (top). According to the $\chi$ (susceptibility) versus $T$ (temperature) plot, the material underwent a ferromagnetic ordering at ~95 K with a small divergence in the ZFC and FC curves below 95 K, Fig. 4.9 (top). The $\chi T$ plot in Fig. 4.10 (top) remains constant in the range of 300 to ~160 K and then undergoes a sharp increase, further supporting the presence of a ferromagnetic component. The field dependence of the magnetization of CuIn$_{0.875}$Fe$_{0.125}$S$_2$ at 2 K is depicted in Fig. 4.11 (top). This shows a magnetic hysteresis with a coercive field of $H_c = 150$ Oe; saturation of the magnetization was not observed.

Figure 4.10: $\chi T$ vs. temperature plot for CuIn$_{0.875}$Fe$_{0.125}$S$_2$ (Top) and CuIn$_{0.85}$Fe$_{0.15}$S$_2$ (Bottom).
Figure 4.11: Top: Field dependence of the magnetization of CuIn$_{0.85}$Fe$_{0.15}$S$_2$ measured at 2 K. The inset shows -0.5 to 0.5 T range. Bottom: Field dependence of the magnetization of CuIn$_{0.875}$Fe$_{0.125}$S$_2$ measured at 2 K. The inset shows -0.3 to 0.3 T range.
It is believed that clustering of the Fe$^{3+}$ ions in the $x = 0.125$ sample gives rise to ferromagnetism at low temperature. Although powder diffraction techniques indicated that iron was being substituted on the indium site of CuInS$_2$, previous Mössbauer spectroscopic data were indicative of Fe$^{3+}$ being present in two unique environments. For samples where $x = 0 - 0.125$ the second type of Fe$^{3+}$ increased with increasing iron content. These results suggest that the solid solution was not completely random throughout the sample and that a clustering of the Fe$^{3+}$ ions was likely present. This clustering is thought to be the origin of the ferromagnetic behavior. A similar argument has been proposed by Popov et al. in the study of CuFeS$_2$, which is known to be antiferromagnetic; however, clustering of the iron is believed to give rise to the ferromagnetic component which appeared below 130 K.$^{198}$ Likewise in a recent study by Lyubutin and coworkers, nanobricks of CuFeS$_2$ were shown to display ferromagnetic behavior below 60 K and one possible explanation was the presence of ferromagnetic clusters arising from a disorder of copper and iron atoms.$^{199}$

The $\chi^{-1}$ (inverse molar susceptibility) versus $T$ (temperature) plot for CuIn$_{0.85}$Fe$_{0.15}$S$_2$ (Fig. 4.9, bottom), is more complicated and displays a significant susceptibility increase in the temperature range of 130 K to 2 K. Examination of the ZFC and FC curves indicates divergence around 80 K indicating a ferromagnetic component and a later upturn in the susceptibility at lower temperature possibly due to a paramagnetic or antiferromagnetic component. This is further supported by the $\chi T$ vs $T$ plot (Fig. 4.10, bottom) which exhibits a continuous decrease from 300 K to ~130 K, suggesting a dominant antiferromagnetic component. Upon further cooling, there is a rapid increase in $\chi T$ vs $T$, supporting the ferromagnetic component. The field dependence of the magnetization of CuIn$_{0.85}$Fe$_{0.15}$S$_2$ at 2 K shows a magnetic hysteresis with a coercive field, $H_c = 500$ Oe (Fig. 4.11). Saturation of the magnetization was not observed.
This phenomenon can be explained based on the X-ray and neutron diffraction data as well as previous Mössbauer results.\textsuperscript{175} The Rietveld refinements of the X-ray and neutron diffraction data revealed a secondary phase for the $x = 0.15$ sample. Additionally, Mössbauer spectroscopic data indicated a significant decrease in the amount of the second type of Fe\textsuperscript{3+} in comparison to the $x = 0.125$ sample. The magnetism of the $x = 0.15$ sample may be explained by the combination of the ferromagnetic clustering similar to $x = 0.125$ sample, to a lesser extent, combined with an iron-containing secondary phase, which lends the antiferromagnetic component. This secondary phase has not been definitively identified; but, it is believed to be cubic-CuIn\textsubscript{1-x}Fe\textsubscript{x}S\textsubscript{2} based on the diffraction data. A similar phenomenon was observed in Teranishi’s work where a tetragonal FeS secondary phase, added a paramagnetic component to the measured susceptibility of CuFeS\textsubscript{2}.\textsuperscript{200} It should also be noted that the $x = 0.125$ and $x = 0.15$ samples both have a calculated $\mu_{\text{eff}}$ (Table 4.4) below that of the ideal Fe\textsuperscript{3+}. As iron has already been determined to be in the 3+ oxidation state, these lower values are indicative of the $d$-electrons of the Fe participating in greater covalent bonding with the sulfur.\textsuperscript{200}

Table 4.4: The Weiss temperature, $\theta$, effective magnetic moment, $\mu_{\text{eff}}$, and Curie constant, $C$, for CuIn\textsubscript{1-x}Fe\textsubscript{x}S\textsubscript{2}.

<table>
<thead>
<tr>
<th>Fe Content (x=)</th>
<th>$\theta$ (K)</th>
<th>$\mu_{\text{eff}}$ ($\mu_B$)</th>
<th>$C$(emuK$^{-1}$mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>-141(2)</td>
<td>5.9(5)</td>
<td>4.43(3)</td>
</tr>
<tr>
<td>0.10</td>
<td>-213(3)</td>
<td>5.4(5)</td>
<td>3.68(3)</td>
</tr>
<tr>
<td>0.125</td>
<td>-120(3)</td>
<td>4.9(4)</td>
<td>2.99(2)</td>
</tr>
<tr>
<td>0.15</td>
<td>-198(2)</td>
<td>5.3(4)</td>
<td>3.55(2)</td>
</tr>
</tbody>
</table>
4.4 Conclusion

Careful analysis using advanced structural characterization techniques of synchrotron X-ray powder diffraction and Neutron powder diffraction revealed the $x = 0.125$ sample to represent the greatest amount of iron that can be incorporated in $\text{CuIn}_{1-x}\text{Fe}_x\text{S}_2$ and the material remain phase pure. At this concentration of Fe, the sample became ferromagnetic and had the highest ZT value of the series. While the $\text{CuIn}_{0.875}\text{Fe}_{0.125}\text{FeS}_2$ sample seems attractive for its combination of semiconducting and ferromagnetic properties, it is limited in its application due to the very low $T_c$ value that we are not able to tune with dopant concentration due to being at the solid solubility limit. The impurity in the $x = 0.15$ sample cause it to exhibit anomalous magnetic behavior and not follow trends in thermopower and thermal conductivity.

The ZT has been enhanced in two different chalcopyrite systems, $\text{CuInS}_2$ reported here and $\text{CuInSe}_2$.\textsuperscript{172, 201} Interestingly, an increase in electrical conductivity and thermopower was observed for both systems with a corresponding favorable decrease in the thermal conductivity, although the type (Fe or Mn), oxidation state, and location of the substituent was different. These data indicate that there must be several ways to improve the ZT in chalcopyrites. The current struggle with these materials is not being able to increase the carrier concentration enough to raise the electrical conductivity toward the Mott minimum metallic conductivity, and it has recently been proposed that significantly exceeding this value is a necessary prerequisite for promising thermoelectric materials.\textsuperscript{202} However, we propose that the type of substitutions studied here may be better used to optimize the ZT when starting with a more promising parent diamond-like material and/or using co-substitution to improve the properties.
4.5 References


Popov, V.V.; Kizhaev, S.A.; Rud, Y.V. Phys Solid State 2011, 53, 71-75.


5 Tuning the Band Gap of CuInS$_2$ Through Lithium and Iron Substitution

5.1 Introduction

Diamond-like semiconductors (DLSs), such as CuInS$_2$, are an attractive class of materials to study. The physicochemical properties can often be tuned via cation substitution, or heavy doping of the compounds, as well as cross-substitution of the cations that results in ternary or quaternary compounds derived from binary DLSs.\textsuperscript{203,204}

Figure 5.1: Left: CuInS$_2$, I-42d structure as viewed down the crystallographic $b$-axis.\textsuperscript{227} Right: Li$_2$FeS$_2$, P-3m1 structure as viewed down the crystallographic $b$-axis.\textsuperscript{205}
CuInS$_2$-based compounds hold promise in potential applications such as thermoelectrics, nonlinear optics, spintronics and light emitting diodes. Of more interest is the photovoltaic properties of CuInS$_2$-based materials which are currently being used in thin film solar cells. In our earlier work (see chapter 3) we replaced some of the expensive and scarce indium with a more affordable and readily abundant element, iron; however, this substitution had a detrimental effect on the band gap energy.

The optical band gap of CuInS$_2$ is reported as 1.53 eV (811 nm) which lies in the infrared region and is in the optimal range for solar energy conversion. Iron was incorporated into this material; unfortunately, CuIn$_{1-x}$Fe$_x$S$_2$ (where x = 0.05-0.15) materials exhibit band gaps deeper in the infrared region at ~0.70 eV – 1.07 eV (1160 - 1773 nm), which is much closer to the CuFeS$_2$ end member (0.60 eV, 2068 nm), than that of CuInS$_2$. This decrease in the band gap makes the CuFeS$_2$-CuInS$_2$ solid solution a less than viable solar cell material as the band gaps lie below the minimum optimum band gap of 1.1 eV (1128 nm). LiInS$_2$ is a related diamond-like semiconductor which has a reported band gap of 3.57 eV (348 nm), which is in the ultra violet region and is significantly higher than that of CuInS$_2$. So it is chemically reasonable to assume that the addition of lithium in both CuInS$_2$ and Fe-substituted CuInS$_2$ should result in an increase of band gap, and may allow these chalcopyrite phases with less indium to be recognized as viable photovoltaic materials.

It is not yet possible to exactly predict what the magnitude of the band gap of a solid solution member will be, only that it will lie somewhere between that of its two end
members. While band structure calculations provide important qualitative information regarding the nature of the band gaps (direct or indirect, etc.), they fall short of the ability to predict the band gaps of materials.\textsuperscript{217} As an example, the calculated band gap for LiInS\textsubscript{2} is 3.17 eV, an underestimation of 11\%.\textsuperscript{218}

Very little work has been done regarding Li-substitution of DLSs, the majority of the Li-substitution studies focus on oxide materials with various structure types. Heikes’ work on Li-substituted transition metal oxides and Hagel’s study on Li-substituted Cr\textsubscript{2}O\textsubscript{3}, a semiconducting oxide, have found that Li-substitution is successful at reducing the resistivity, hence increasing the conductivity of the materials being studied.\textsuperscript{219,220} The Li-N-codoping of ZnO has been explored by Yamamoto, and has produced \textit{p}-type crystals with low resistivity.\textsuperscript{221} Li-doping has also been employed to engineer defects (holes) in ZnO in order to tune the ferromagnetism of the material.\textsuperscript{222} The closest research to that being undertaken in this study is the work of Weise\textsuperscript{223} and that of Batchelor.\textsuperscript{205} Weise studied the selenium counterpart in his work on the Cu\textsubscript{1-x}Li\textsubscript{x}InSe\textsubscript{2} series, finding that the materials maintained the chalcopyrite structure with as much as x = 0.55 Li content.\textsuperscript{223} However, Weise finds that the resistivity increases with increasing amounts of Li-substitution. Studies have been undertaken, by Batchelor and others, on the Li\textsubscript{2-x}Cu\textsubscript{x}FeS\textsubscript{2} series, which crystallizes in the space group P-3\textit{m}1.\textsuperscript{205,224} These studies focus on Li ion conductivity and the solubility limit of Cu on the Li site, where it is verified that samples with x \leq 1 (LiCuFeS\textsubscript{2}) are isostructural with Li\textsubscript{2}FeS\textsubscript{2}.\textsuperscript{225,224}

DLSs are named such, as their structures are derived from either the hexagonal or cubic form of diamond.\textsuperscript{226} The tetragonal, chalcopyrite structure of CuInS\textsubscript{2} is an ordered superstructure of the cubic zinc blende structure. CuInS\textsubscript{2} crystallizes in the space group
I-42d (Fig. 5.1), in which the copper occupies the 4a site, the indium the 4b, and the sulfur occupies the 8d site. Trivalent iron has been shown to successfully incorporate into the structure as described in detail in chapter 3, up to the nominal composition of CuIn$_{0.875}$Fe$_{0.125}$S$_2$, and occupy the 4b site. The incorporation of Fe in the In site was not a surprise, as CuFeS$_2$, chalcopyrite, also crystallizes in the I-42d space group. Although a diamond-like semiconductor, LiInS$_2$ does not crystallize in the I-42d space group, but in the Pna2$_1$ space group. This makes it difficult to predict whether Li can be successfully substituted for Cu in CuInS$_2$, while still maintaining the I-42d space group. Despite the fact that LiInSe$_2$ crystallizes in the Pna2$_1$ space group, Weise’s successful study of the Li-substituted CuInSe$_2$, which also crystallizes in the I-42d space group, indicates that Li most likely can be substituted for Cu in CuInS$_2$, to some extent, and it will still maintain the I-42d space group. Upon the addition of lithium, CuInS$_2$ and CuIn$_{1-x}$Fe$_x$S$_2$ may crystallize in the I-42d space group, the Pna2$_1$ space group, a mixture of phases, or another phase, based on Li$_2$FeS$_2$ for example could be established. The Li$_2$FeS$_2$, P-3m1, structure is quite different from the chalcopyrite-like structure of CuInS$_2$, as can be evidenced in the Li$_2$FeS$_2$ structure in Figure 5.1. This structure is a layered two-dimensional structure, as opposed to the more tightly packed three dimensional chalcopyrite structure (Figure 5.1). The Li$_2$FeS$_2$ structure consists of [LiFeS$_2$]$^-$ layers separated by Li$^+$ cations. There is one metal site in the layers which is tetrahedral and occupied 50% by Fe$^{2+}$ and 50% by Li$^+$. The lithium cation between the layers resides in an octahedral pocket of S$^{2-}$ anions.

This work will explore the solubility limit of Li in both CuInS$_2$ and Fe-substituted CuInS$_2$, and the effects that the substitution and cosubstitution have on the optical band
gap of the materials. This work is valuable because, despite being investigated for a wide variety of physicochemical properties, little is known about the structure-property relationships among DLSs. To the authors’ knowledge, there are no studies of the Li-substitution of Cu in either CuInS$_2$ or Fe-substituted CuInS$_2$ that have been undertaken. Here, the effects of lithium substitution in both CuInS$_2$ and CuIn$_{0.90}$Fe$_{0.10}$S$_2$, on the structure and physicochemical properties, will be determined using several characterization techniques. X-ray powder diffraction data combined with Reitveld refinement, inductively coupled plasma spectrometry, and optical band gap estimations of both series will be reported and discussed. This study is being undertaken to better elucidate structure-property relationships, both electronic and crystal structure, in the Li-Fe-substituted CuInS$_2$ series.

5.2 Experimental

5.2.1 Reagents

The chemicals in this work were used as obtained: (1) lithium sulfide powder, 98%- 99.9% Li, Strem Chemicals Inc. (Newburyport, MA, USA); (2) copper: 100 mesh, 99.999%, Strem Chemicals Inc. (Newburyport, MA, USA); (3) indium: 325 mesh, 99.99%, Strem Chemicals Inc. (Newburyport, MA, USA); (4) iron: 22 mesh, 99.99%, Strem Chemicals Inc. (Newburyport, MA, USA); (5) sulfur, sublimed powder, 99.5%, Fisher Scientific (Pittsburgh, PA, USA).
5.2.2 Synthesis

High-temperature, solid-state synthesis of the Li-substituted CuInS$_2$ and the Li-substituted CuIn$_{0.90}$Fe$_{0.10}$S$_2$ series involved an intricate heating profile adapted from Weise’s Cu$_{1-x}$Li$_x$InSe$_2$ study.$^{223}$ Lithium sulfide, copper, indium, sulfur, and when intended, iron were combined in stoichiometric amounts in an argon-filled glove box. Each sample was inserted in a 9 mm od graphite tube, which was then placed in a fused-silica tube (12 mm od). The tubes were then transferred to a vacuum line, held under a vacuum of 10$^{-4}$ mbar and flamed-sealed with the use of a gas/oxygen torch. The sealed tubes were then transferred to a computer-controlled furnace, where they were heated up to 1150 °C, Figure 5.2. The resulting ingots, which were a dark grey in color, were viewed under an optical microscope and ground into a fine powder for further characterization.
Figure 5.2: Heating profile for both Cu$_{1-x}$Li$_x$InS$_2$ and Cu$_{1-x}$Li$_x$In$_{0.90}$Fe$_{0.10}$S$_2$ series.

5.2.3 X-ray Powder Diffraction and Rietveld Refinement

Each sample was ground with an internal standard (High-purity silicon, NIST) for 50 min, using an agate mortar and pestle. The samples were then backfilled into the aluminum sample holders. A PANalytical X’Pert Pro MPD X-ray powder diffractometer equipped with an X’Celerator detector, copper K$_\alpha$ radiation with a wavelength of 1.54187 Å, a tube amperage of 40 mA, and a voltage of 45 kV, was used to collect the X-ray powder diffraction data. The instrument was fitted with a 1/4° divergence slit, 1/2° anti-scatter slit, and a 0.02 rad soller slit at both the diffracted and incident beams. The data were collected from 10 to 145° 2θ, with a scan speed of 0.010644 °/s, and a step size of
0.008°. Crystalline phase identification was enabled with the use of the search and match capabilities of the X’Pert HighScore Plus program, along with the International Centre for Diffraction Data (ICDD) powder diffraction file (PDF) database.²³¹

GSAS, along with the EXPGUI interface, was employed in order to perform Rietveld refinements of the X-ray powder diffraction data.²³²,²³³ A Pseudo-Voight function in conjunction with a Finger-Cox-Jephcoat asymmetry correction was used to model the peak profile. The background was refined using a shifted Chebyshev type (12 to 18 terms).²³⁴ The following were refined: lattice parameters, background parameters, atomic coordinates, site occupancy, and isotropic atomic displacement parameters. When an attempt was made to refine: (1) Li on the In(4b) site, (2) Fe on the Cu(4a) site, or (3) to let all of the cations refine freely, the R factors increased and negative atomic displacement parameters for both Fe and Cu were a result; therefore these models were rejected. The final model that was employed included refining Fe on the In(4b) site first (when refining the Cu₁₋ₓLiₓIn₀.₉₀Fe₀.₁₀S₂ models), fixing the refined values, and then refining Li on the Cu(4a) site. This model provided results that made the most chemical sense, and was employed in the refinement of all samples.

5.2.4 Optical Diffuse Reflectance UV/Vis/NIR Spectroscopy

A Cary 5000 UV/Vis/NIR spectrometer, equipped with a Harrick Praying Mantis diffuse reflectance accessory that uses elliptical mirrors to focus the beam, was employed to collect the optical diffuse reflectance spectra. The 100% reflectance standard used was BaSO₄ (Fisher, 99.92%). The powdered samples were placed into the sample holders and inserted into the instrument, where scans were performed from 200 nm to 2500 nm. The
energy (eV) was calculated from the wavelength (\( \lambda \)), and the percent reflectance data were converted to absorption using the Kubelka-Munk equation.\(^{235}\) The addition of a correction factor was needed to realign the discontinuities in the plotted data resulting from the detector changes. The absorption edges, for all but the undoped sample, exhibited shoulders resulting from doping.\(^{236}\) The complexity in the Urbach tails made it difficult to estimate the band gap (\( E_g \)) as they were estimated in chapter 3. In order to account for the complexity of the curves, a line of best fit is drawn along the steepest slope of the absorption edge. The band gap is then estimated from the midpoint of the line that is tangent to the curve. Because of the simplicity of the absorption edge of the undoped sample, there is no change in the band gap when treated in this manner. In the Fe-substituted sample, the reported band gap here is higher than that reported in chapter 3 because of the difference in band gap treatment. However, this treatment allows for a consistent estimation of the band gap in data that displays complex Urbach tails.

### 5.2.5 Inductively Coupled Plasma

Inductively coupled plasma optical emission spectrometry (ICP-OES) was performed by RJ Lee Group, Inc. (Monroeville, PA), operating in accordance with ISO 17025:2005 guidelines, as a means of quantitative analysis of the copper, lithium, indium, iron, and sulfur. Using high pressure XP1500 vessels in a MarsExpress CEM Microwave system, the samples were digested with trace metal nitric acid (Fisher Scientific). The samples were held at 180°C for twenty min. A Varian 730ES ICP-OES was then utilized to analyze the digested samples.
5.3 Results & Discussion

5.3.1 X-ray Powder Diffraction and Rietveld Refinement

A series of $\text{Cu}_{1-x}\text{Li}_x\text{InS}_2$ samples were prepared up to $x = 0.40$. Samples where $x \leq 0.30$ appeared to be phase pure upon the initial inspection of the X-ray powder diffraction data. The diffraction pattern for the sample where $x = 0.40$, had peaks that could not be indexed to the $\text{CuInS}_2$ tetragonal, $I-42d$ phase. These peaks were attributed to a secondary phase of $\text{In}_2\text{S}_3$ ($I_41/a$).\textsuperscript{237} Rietveld refinements were performed for samples where $x = 0.05$, 0.10, 0.20, and 0.30. When Li was added to the Cu 4a site, the SOF(Li) refined well and was in good agreement with the intended stoichiometry, as can be seen in Table 5.1. Satisfactory results could not be obtained when using other models as described in more detail in section 5.2.3. All refinements had $\chi^2$ values less than 2 (Table 5.1), and excellent graphical fits of the calculated pattern to the observed data, as can be evidenced in the difference plots in Figure 5.3. All of the models for $\text{Cu}_{1-x}\text{Li}_x\text{InS}_2$ refined well and suggest that lithium is successfully incorporating into the copper site.
Table 5.1: Rietveld refinement results for X-ray powder diffraction data obtained for Cu$_{1-x}$Li$_x$InS$_2$, where $x = 0$-0.30.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>x=0.05</th>
<th>x=0.10</th>
<th>x=0.20</th>
<th>x=0.30</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$(Å)</td>
<td>5.5276(6)</td>
<td>5.53268(5)</td>
<td>5.54736(6)</td>
<td>5.55556(7)</td>
</tr>
<tr>
<td>$c$(Å)</td>
<td>11.1477(2)</td>
<td>11.1470(2)</td>
<td>11.1556(2)</td>
<td>11.1580(3)</td>
</tr>
<tr>
<td>Cell Volume(Å$^3$)</td>
<td>340.614(9)</td>
<td>341.216(7)</td>
<td>343.293(8)</td>
<td>344.38(1)</td>
</tr>
<tr>
<td>$c/a$ ratio</td>
<td>2.017</td>
<td>2.015</td>
<td>2.011</td>
<td>2.008</td>
</tr>
</tbody>
</table>

**Cation 4a (Cu/Li)**

| SOF                      | 0.9396(2)/0.0604(2) | 0.9012(2)/0.0988(2) | 0.7974(2)/0.2026(2) | 0.7163(2)/0.2837(2) |
| $100U_{iso}$(Å$^2$)      | 1.98(7)         | 2.40(8)        | 2.27(8)        | 2.29(9)        |

**Cation 4b (In)**

| SOF                      | 1.00           | 1.00           | 1.00           | 1.00           |
| $100U_{iso}$(Å$^2$)      | 1.17(3)        | 1.56(4)        | 1.95(4)        | 1.29(3)        |

**Anion 8d (S)**

| SOF                      | 1.00           | 1.00           | 1.00           | 1.00           |
| $100U_{iso}$(Å$^2$)      | 2.11(8)        | 2.8(1)         | 2.86(9)        | 1.75(8)        |
| $X_s$                    | 0.2358(6)      | 0.2355(8)      | 0.2458(6)      | 0.2418(6)      |
| $\chi^2$                | 1.761          | 1.993          | 1.994          | 1.978          |
| $wR_p$                   | 0.0579         | 0.0626         | 0.0638         | 0.0640         |
Figure 5.3: Rietveld refinement results using X-ray powder diffraction data for Cu$_{1-x}$Li$_x$InS$_2$. Observed (+++) and calculated (red solid line) X-ray powder diffraction patterns are on top. The difference is shown in the plot on the bottom. The two sets of tick marks indicate the expected Bragg reflections of Si and the refined model.

The Li-substituted CuIn$_{0.90}$Fe$_{0.10}$S$_2$ samples were treated exactly as the iron-free Cu$_{1-x}$Li$_x$InS$_2$ samples. As in the Cu$_{1-x}$Li$_x$InS$_2$ series, the Cu$_{1-x}$Li$_x$In$_{0.90}$Fe$_{0.10}$S$_2$ series was phase pure up to $x \leq 0.30$, after which a secondary cubic phase was observable.$^{238}$ Interestingly, this was the same secondary phase that was observed in the CuIn$_{0.85}$Fe$_{0.15}$S$_2$ sample once the iron reached its solubility limit. In the Li-substituted CuIn$_{1-x}$Fe$_x$S$_2$ series$^{228}$, the iron resides on the indium, 4b, site and the lithium resides on the copper, 4a
site. The final refinement provided both iron and lithium site occupation factors that matched well with the nominal composition (Table 5.2). These results also agreed well with the ICP data (Table 5.3), which confirmed that lithium was present in all of the samples in quantities that are in accordance with the intended stoichiometry. The difference plots for samples where \( x = 0.05, 0.10, 0.20, \) and \( 0.30 \) can be seen in Figure 5.4. The graphical fits combined with the favorable reliability factors (\( \chi^2 \) less than 2), indicate that lithium substitution into the copper site was achieved, and iron was successfully incorporated into the indium site. The high solubility limit of Li in both the \( \text{Cu}_{1-x}\text{Li}_x\text{InS}_2 \) and the \( \text{Cu}_{1-x}\text{Li}_x\text{In}_{0.90}\text{Fe}_{0.10}\text{S}_2 \) series is not surprising considering that \( \text{LiInSe}_2 \) is isostructural to \( \text{LiInS}_2 \), and Weise found that \( \text{CuInSe}_2 \) could be substituted with up to 55% \( \text{Li} \) and maintain the structure of the parent compound.

**Table 5.2: Rietveld refinement results for X-ray powder diffraction data from \( \text{Cu}_{1-x}\text{Li}_x\text{In}_{0.90}\text{Fe}_{0.10}\text{S}_2 \), where \( x = 0 - 0.30 \).**

<table>
<thead>
<tr>
<th>Parameters</th>
<th>( x=0.05 )</th>
<th>( x=0.10 )</th>
<th>( x=0.20 )</th>
<th>( x=0.30 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( a(\text{Å}) )</td>
<td>5.51290(5)</td>
<td>5.52022(5)</td>
<td>5.53262(6)</td>
<td>5.54762(8)</td>
</tr>
<tr>
<td>( c(\text{Å}) )</td>
<td>11.1073(2)</td>
<td>11.1164(2)</td>
<td>11.1250(2)</td>
<td>11.1304(3)</td>
</tr>
<tr>
<td>Cell Volume(Å(^3))</td>
<td>337.575(8)</td>
<td>338.749(8)</td>
<td>340.564(9)</td>
<td>342.55(1)</td>
</tr>
<tr>
<td>( c/a ) ratio</td>
<td>2.015</td>
<td>2.014</td>
<td>2.011</td>
<td>2.006</td>
</tr>
</tbody>
</table>

**Cation 4a (Cu/Li)**

<table>
<thead>
<tr>
<th>( 100U_{iso}(\text{Å}^2) )</th>
<th>0.9404(1)/0.0596(1)</th>
<th>0.8888(1)/0.1112(1)</th>
<th>0.8323(1)/0.1677(1)</th>
<th>0.7009(2)/0.2991(2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 100U_{iso}(\text{Å}^2) )</td>
<td>1.46(8)</td>
<td>2.58(9)</td>
<td>2.01(6)</td>
<td>2.37(8)</td>
</tr>
</tbody>
</table>

**Cation 4b (In/Fe)**

<table>
<thead>
<tr>
<th>( 100U_{iso}(\text{Å}^2) )</th>
<th>0.8922(3)/0.1078(3)</th>
<th>0.8997(1)/0.1003(1)</th>
<th>0.8855(1)/0.1145(0)</th>
<th>0.8890(2)/0.1110(1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 100U_{iso}(\text{Å}^2) )</td>
<td>1.76(6)</td>
<td>1.52(4)</td>
<td>1.58(2)</td>
<td>1.48(3)</td>
</tr>
</tbody>
</table>

**Anion 8d (S)**

<table>
<thead>
<tr>
<th>( 100U_{iso}(\text{Å}^2) )</th>
<th>1.00</th>
<th>1.00</th>
<th>1.00</th>
<th>1.00</th>
</tr>
</thead>
<tbody>
<tr>
<td>( X_s )</td>
<td>0.2217(7)</td>
<td>0.2412(7)</td>
<td>0.2418(5)</td>
<td>0.2404(6)</td>
</tr>
<tr>
<td>( \chi^2 )</td>
<td>1.976</td>
<td>1.975</td>
<td>1.321</td>
<td>1.771</td>
</tr>
<tr>
<td>( wR_p )</td>
<td>0.0608</td>
<td>0.0618</td>
<td>0.0486</td>
<td>0.0596</td>
</tr>
</tbody>
</table>
Table 5.3: Chemical composition of Cu_{1-x}Li_xInS_2 and Cu_{1-x}Li_xIn_{0.90}Fe_{0.10}S_2, where x = 0.10 - 0.30, measured by ICP. These formulae are normalized using the expected sulfur content.

<table>
<thead>
<tr>
<th>x, Intended Li Content</th>
<th>Li</th>
<th>Cu</th>
<th>In</th>
<th>Fe</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.10</td>
<td>0.096</td>
<td>0.929</td>
<td>0.981</td>
<td>0</td>
<td>2.00</td>
</tr>
<tr>
<td>0.20</td>
<td>0.222</td>
<td>0.838</td>
<td>1.012</td>
<td>0</td>
<td>2.00</td>
</tr>
<tr>
<td>0.30</td>
<td>0.287</td>
<td>0.787</td>
<td>1.017</td>
<td>0</td>
<td>2.00</td>
</tr>
<tr>
<td>0.10</td>
<td>0.091</td>
<td>0.986</td>
<td>0.935</td>
<td>0.093</td>
<td>2.00</td>
</tr>
<tr>
<td>0.20</td>
<td>0.181</td>
<td>0.839</td>
<td>0.969</td>
<td>0.098</td>
<td>2.00</td>
</tr>
<tr>
<td>0.30</td>
<td>0.301</td>
<td>0.756</td>
<td>0.977</td>
<td>0.086</td>
<td>2.00</td>
</tr>
</tbody>
</table>

In the initial Fe-substituted CuInS_2 series, it was found that the unit cell volume and lattice parameters decreased, in a linear fashion, with increasing amounts of Fe-substitution.\textsuperscript{213} This was to be expected, as the crystal radius of four-coordinate Fe\textsuperscript{3+} is 0.63 Å, notably smaller than that of four-coordinate In\textsuperscript{3+} or Cu\textsuperscript{+} (0.76 and 0.74 Å, respectively).\textsuperscript{239} In the case of Li-substituted Cu_{1-x}Li_xInS_2 and Cu_{1-x}Li_xIn_{0.90}Fe_{0.10}S_2, an analysis of the lattice parameters revealed that the a-axis increased, linearly, with increasing amounts of Li-substitution (Figure 5.5 top). The c-axis also increased with increasing amounts of Li-substitution for both series, however, not in a linear fashion (Figure 5.5 bottom). The lack of linearity in the c-axis vs. Li content, according to Vegard’s Law,\textsuperscript{240} suggested that the lithium ions may not be randomly distributed on the 4a site throughout the crystal structure. The iron in the previously reported CuIn_{1-x}Fe_xS_2 series was suspected to form clusters, as opposed to being randomly distributed, and the clustering amount increased with increasing dopant concentration, as suggested by \textsuperscript{57}Fe Mössbauer studies.\textsuperscript{228}
Figure 5.4: Rietveld refinement results using X-ray powder diffraction data for Cu$_{1-x}$Li$_x$In$_{0.90}$Fe$_{0.10}$S$_2$. Observed (+++) and calculated (red solid line) X-ray powder diffraction patterns are on top. The difference is shown in the plot on the bottom. The two sets of tick marks indicate the expected Bragg reflections of Si and the refined model.
Figure 5.5: Top: Refined lattice parameter $a$ for both $\text{Cu}_{1-x}\text{Li}_x\text{InS}_2$ and $\text{Cu}_{1-x}\text{Li}_x\text{In}_{0.90}\text{Fe}_{0.10}\text{S}_2$, where $x = 0.05-0.30$, versus lithium concentration. Bottom: Refined lattice parameter $c$ for both $\text{Cu}_{1-x}\text{Li}_x\text{InS}_2$ and $\text{Cu}_{1-x}\text{Li}_x\text{In}_{0.90}\text{Fe}_{0.10}\text{S}_2$, where $x = 0.05-0.30$. Note that the error bars are omitted as they were not distinguishable from the data point markers.
The binary zinc blende parent compound is cubic with a ratio of the lattice parameters $c/a = 1$. The tetragonal chalcopyrite structure is a super structure of the zinc blende and if the $c$ axis were simply doubled the $c/a$ ratio would equal 2; however this is usually not the case for chalcopyrites. The difference of the $c/a$ ratio from the ideal of 2 is often referred to as the tetragonal distortion, which results from an unequal bond distance between sulfur and the two cations (bond alternation). Interestingly, the $c/a$ ratio (Table 5.1 and 5.2) for both series decreased with increasing amounts of Li-substitution (Fig 5.6). As the $c/a$ ratio decreased, the tetragonal structure became less distorted (as evidenced also in the $x_s$ values). This trend was observed upon iron substitution in the CuInS$_2$ series, in the $x = 0.05 – 0.125$ samples, but by such small increments that the change was essentially negligible.$^{213}$
Figure 5.6: The c/a ratio vs lithium content for both series, Cu$_{1-x}$Li$_x$InS$_2$ and Cu$_{1-x}$Li$_x$In$_{0.90}$Fe$_{0.10}$S$_2$, where x = 0.05-0.30. The data point for the x = 0.20 samples are nearly on top of one another.
Figure 5.7: Refined cell volumes for both Cu$_{1-x}$Li$_x$InS$_2$ and Cu$_{1-x}$Li$_x$In$_{0.90}$Fe$_{0.10}$S$_2$, where $x = 0.05$-$0.30$, versus lithium concentration. Note that the error bars are omitted as they were not distinguishable from the data point markers.

The cell volumes for both of the Cu$_{1-x}$Li$_x$InS$_2$ and the Cu$_{1-x}$Li$_x$In$_{0.90}$Fe$_{0.10}$S$_2$ series increase in a linear fashion, as can be seen in Figure 5.7. This increase cannot be explained in terms of crystal radii as Li$^+$ has a similar crystal radius relative to Cu$^+$ and In$^{3+}$(0.73, 0.74, and 0.76 Å respectively).$^{239}$ The increase stems from a change in bond lengths due to the fact that a Li-S bond is longer than that of Cu-S and In-S bonds. In the undoped chalcopyrite structure, the sulfur anion is displaced from the ideal zinc blende position of $x_s = 0.25$ creating a tetragonal distortion because of bond alternation.$^{249}$ In
this chalcopyrite structure, the bond alternation is such that the Cu-S bonds are shorter and the In-S bonds are longer. The decrease in anion displacement in both the Cu$_{1-x}$Li$_x$InS$_2$ and the Cu$_{1-x}$Li$_x$In$_{0.90}$Fe$_{0.10}$S$_2$ series in this work are indicative of the Li/Cu-S bonds elongating and the Fe/In-S bonds shortening (Figure 5.8) as compared to the bond distances in the undoped chalcopyrite structure.

The bond lengths generated from the Rietveld refinement models for the Cu$_{1-x}$Li$_x$InS$_2$ and Cu$_{1-x}$Li$_x$In$_{0.90}$Fe$_{0.10}$S$_2$ series are listed in Table 5.4. Rietveld refinements allow for the refinement of shared site occupancy; however, when the ions are fixed at the same position in the lattice and the associated bond lengths of the ions in the shared

---

Figure 5.8: Top: Depiction of band structure and band gap variation of CuInS$_2$ with Fe- and Li-substitution. Bottom: Bond alternation in CuInS$_2$ and corresponding changes in $x_i$. CB min, VB max, and IB refer to the minimum conduction band, maximum valence band, and intermediate band respectively.
site will be equal therefore; they are reported in this work as the Li/Cu-S and Fe/In-S bond. The Cu-S bond distance of 2.325(2) Å in the CuInS₂ sample is comparable with other published works of CuInS₂, with Cu-S bond lengths ranging from 2.28 – 2.33 Å.²⁴³,²⁴⁴,²⁴⁵ LiInS₂ has a reported Li-S bond of 2.49 Å,²⁴⁶ so it was no surprise that upon Li-substitution, the Li/Cu-S bond distance increases due to the greater ionicity of the Li-S bond as compared to the Cu-S bond. In Cu₁₋ₓLiₓInS₂ samples, where x = 0.05-0.10, the Li/Cu-S bond increases from the parent, CuInS₂, by 0.031 Å for each sample. However, the Li/Cu-S bond distance is greater for the x = 0.20 sample than it is for the x = 0.30 sample, with Li/Cu-S bond distances of 2.393(2) Å at 2.383(2) Å, respectively. Although the trend is nonlinear, all of the Li/Cu-S bond distances in the Li-doped compounds are longer than the Cu-S distance in the CuInS₂ end member. For comparison, the Li-S distances in Li₂FeS₂ range from 2.41-2.44 Å for the tetrahedrally coordinated lithium cation in the layers, to 2.71-2.74 Å for the lithium cation that resides between the layers.²⁰⁵,²⁴⁷

The In-S bond distances in the Cu₁₋ₓLiₓInS₂ samples decrease with Li-substitution. However, the increase in the Li/Cu-S bond distance is greater than the decrease in In-S bond distance in each of the Cu₁₋ₓLiₓInS₂ samples with the exception of the Cu₀.₉₅Li₀.₀₅InS₂ sample. The decrease of the In-S bond length in this sample is 0.001 Å greater than the increase in the Li/Cu-S bond distance; however, it should be noted that the ESD is ±0.002 Å on each of these bond lengths. The In-S bond distance in the published works for CuInS₂ ranges from 2.46-2.51 Å,²⁴³,²⁴⁴,²⁴⁵ and that in LiInS₂ is reported at 2.51 Å.²¹⁸ Therefore, In-S bond distances in the samples in this work, are
closer to the lower end of the range of In-S bond distances in CuInS$_2$ than to that of LiInS$_2$, with no linear trend associated with the amount of Li-substitution.

Table 5.4: Bond distances generated from Rietveld refinement models

<table>
<thead>
<tr>
<th>Compound</th>
<th>Li/Cu-S bond (Å)</th>
<th>Fe/In-S bond (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuInS$_2$</td>
<td>2.325(2)</td>
<td>2.478(2)</td>
</tr>
<tr>
<td>Cu$<em>{0.95}$Li$</em>{0.05}$InS$_2$</td>
<td>2.356(2)</td>
<td>2.446(2)</td>
</tr>
<tr>
<td>Cu$<em>{0.90}$Li$</em>{0.10}$InS$_2$</td>
<td>2.356(2)</td>
<td>2.449(3)</td>
</tr>
<tr>
<td>Cu$<em>{0.80}$Li$</em>{0.20}$InS$_2$</td>
<td>2.393(2)</td>
<td>2.420(2)</td>
</tr>
<tr>
<td>Cu$<em>{0.70}$Li$</em>{0.30}$InS$_2$</td>
<td>2.383(2)</td>
<td>2.436(2)</td>
</tr>
<tr>
<td>CuIn$<em>{0.90}$Fe$</em>{0.10}$S$_2$</td>
<td>2.324(2)</td>
<td>2.467(2)</td>
</tr>
<tr>
<td>Cu$<em>{0.95}$Li$</em>{0.05}$In$<em>{0.90}$Fe$</em>{0.10}$S$_2$</td>
<td>2.307(2)</td>
<td>2.486(2)</td>
</tr>
<tr>
<td>Cu$<em>{0.90}$Li$</em>{0.10}$In$<em>{0.90}$Fe$</em>{0.10}$S$_2$</td>
<td>2.368(2)</td>
<td>2.424(2)</td>
</tr>
<tr>
<td>Cu$<em>{0.80}$Li$</em>{0.20}$In$<em>{0.90}$Fe$</em>{0.10}$S$_2$</td>
<td>2.374(2)</td>
<td>2.427(2)</td>
</tr>
<tr>
<td>Cu$<em>{0.70}$Li$</em>{0.30}$In$<em>{0.90}$Fe$</em>{0.10}$S$_2$</td>
<td>2.374(2)</td>
<td>2.436(2)</td>
</tr>
</tbody>
</table>

The samples in the Cu$_{1-x}$Li$_x$In$_{0.90}$Fe$_{0.10}$S$_2$ series exhibited a similar trend in Li/Cu-S and Fe/In-S bond distances, with the exception of the x = 0.05 sample. In this sample, the Li/Cu-S bond distance decreased to 2.307(2) Å, but was offset by an even greater increase in the Fe/In-S bond distance (by 0.019 Å). The anion displacement (movement further away from the ideal cubic sulfur atomic position of $x_s = 0.25$) of the x = 0.05 sample was also larger than that of the parent (0.2217 and 0.2296 Å, respectively), indicating an increase in the tetragonal distortion of the structure. This could suggest that the Li was incorporated into the In(4b) site rather than the Cu(4a) site, however this Rietveld refinement model was not successful. There was also a break in the $x_s$ trend in the Cu$_{1-x}$Li$_x$In$_{0.90}$Fe$_{0.10}$S$_2$ series (Table 5.2) where the x = 0.30 samples deviates. This may be due to a minor secondary phase that is not easily distinguished in the XRPD patterns. Unlike the Cu$_{1-x}$Li$_x$In$_{0.90}$Fe$_{0.10}$S$_2$ series, there appears to be a nonlinear trend in
$x_s$ in the Cu$_{1-x}$Li$_x$InS$_2$ series, but the anion displacement decreased for all of the doped compounds (Table 5.1).

The fact that the Cu/Li-S bond distances in the substituted series are longer than the unsubstituted compound and are closer Li-S bond distances, further supports that Li is being successfully incorporated into the chalcopyrite (I-42d) CuInS$_2$ structure. The overall increase in cell volume and lattice parameters, combined with the increase in the Li/Cu-S bond distances also strongly supports the successful incorporation of lithium into Cu$_{1-x}$Li$_x$InS$_2$ and Cu$_{1-x}$Li$_x$In$_{0.90}$Fe$_{0.10}$S$_2$ (where $x = 0.05-0.30$). The anomalies found in the Cu/Li-S and Fe/In-S bond distances, as well as those found in the $x_s$ values may be better explained with a high-quality neutron or synchrotron powder diffraction study.

### 5.3.2 Band Gaps

The band gaps of each member of both the Cu$_{1-x}$Li$_x$InS$_2$ and the Cu$_{1-x}$Li$_x$In$_{0.90}$Fe$_{0.10}$S$_2$ series were estimated using optical diffuse reflectance measurements in the UV/Vis/NIR region. The unsubstituted CuInS$_2$ in this work has a band gap (1.50 eV) only slightly less than that of other published band gaps (1.52 – 1.55 eV).$^{212,248}$ This could be due to the difference in the physical state of the material (powder vs. single crystal), different ways of treating the absorption edge to obtain the band gap value, or different synthetic routes that were taken, etc. In this work, all samples are powdered polycrystalline materials synthesized via direct solid-state synthesis, with a maximum temperature of 1150°C.$^{213}$ The band gaps of the Li-substituted Cu$_{1-x}$Li$_x$InS$_2$ materials all increased (Table 5.5, Fig. 5.9).
Table 5.5: Summary of estimated band gaps from optical diffuse reflectance experiments.

<table>
<thead>
<tr>
<th>Li Content (x = )</th>
<th>Cu$_{1-x}$Li$_x$InS$_2$, Band Gap (eV)</th>
<th>Cu$<em>{1-x}$Li$<em>x$In$</em>{0.90}$Fe$</em>{0.10}$S$_2$, Band Gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.50</td>
<td>1.07</td>
</tr>
<tr>
<td>0.05</td>
<td>1.52</td>
<td>1.27</td>
</tr>
<tr>
<td>0.10</td>
<td>1.56</td>
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<tr>
<td>0.20</td>
<td>1.67</td>
<td>1.40</td>
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<tr>
<td>0.30</td>
<td>1.75</td>
<td>1.34</td>
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</tbody>
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Figure 5.9: Optical diffuse reflectance spectra converted to absorption for Cu$_{1-x}$Li$_x$InS$_2$, where $x = 0 - 0.30$. 
The band gap of the $x = 0.05$ sample increased only slightly from the estimated band gap for the CuInS$_2$ parent compound. The $x = 0.10$ sample has an estimated band gap of 1.56 eV, 4% larger than that of the undoped compound. An ~11% increase in the band gap of the Cu$_{1-x}$Li$_x$InS$_2$ materials was realized in samples where $x = 0.20$, and an ~17% increase is seen in the $x = 0.30$ sample (Table 5.5, Fig. 5.9). These changes in the band gap can be related back to the changes in the crystal structure of the materials as previously discussed and expected changes in the electronic structure.

In order to better understand the changes in the band gap upon Li-substitution, it is important to be familiar with the electronic structures of the parent compounds. The density of states for CuInS$_2$ indicated that the upper limits of the valence band (VB), which ranges from -6 eV – 0 eV, are dominant antibonding orbitals formed by the interaction of the Cu3$d$ and S3$p$. Deeper within the valence band below -6 eV the main contribution to the band structure was the In5$s$ and 5$p$ interactions with the S3$p$ orbitals. As a result, it would be expected that if copper were being replaced it would result in changes near the Fermi level. In a study by Yao et al., in which Cu-vancancies were introduced into CuInSe$_2$ (Cu$_{0.95-x}$Mn$_{0.05}$InSe$_2$, where $x = 0 – 0.20$), a widening of the band gap was observed with decreased copper content, as this reduction in copper resulted in a lessening of the repulsive Cu$d$-Sp interactions within the upper valence band. A density functional theory investigation by Ma et al. revealed that unlike Cu $d$-orbitals in chalcopyrites, the Li $s$ and $p$ orbitals in LiInS$_2$ have very little contribution to the valance band (VB) max and conduction band (CB) min, with the majority of their contribution much lower in the VB (-13 to -11 eV) and higher in the CB (5-8 eV), leading to an increase in the difference between the VB and the CB. The VB
max and CB min in LiInS\textsubscript{2} are instead dominated by the In5s-5p orbitals and the S3p orbitals, which give the In-S bond a stronger covalency than the Li-S bond.\textsuperscript{218,251} In this work it was known that the Li/Cu-S bonds are lengthening, so it was most likely that as these atoms moved further apart lessening the antibonding Cu3d – S3p interactions near the VB max and CB min this resulted in a lower band dispersion and thus a larger band gap (Figure 5.8).

In the case of the Cu\textsubscript{1-x}Li\textsubscript{x}In\textsubscript{0.90}Fe\textsubscript{0.10}S\textsubscript{2} materials the effects of Li-substitution on the electronic structure were similar to those found in the Cu\textsubscript{1-x}Li\textsubscript{x}InS\textsubscript{2} series (Table 5.5, Figure 5.10), but a bit more complex due to the addition of Fe. As described in chapter 2, Fe-substitution decreases the band gap of CuInS\textsubscript{2} by ~29%. The band gap was estimated to be 1.07 eV, which is just out of the ideal range for a useful photovoltaic material. This drastic reduction in the band gap of this semiconductor was predicted in the theoretical study conducted by Tablero.\textsuperscript{252} Tablero found that an intermediate band is situated above the valence band in an Fe-substituted material. This intermediate band (IB) acted as an acceptor band (as it was empty), was comprised of the 3d-Fe orbitals and lay at ~0.8 – 1.0 eV above the valence band.\textsuperscript{252} However, it was found that with a minimal amount of Li-substitution (x = 0.05) in the Cu\textsubscript{1-x}Li\textsubscript{x}In\textsubscript{0.90}Fe\textsubscript{0.10}S\textsubscript{2} materials, the band gap immediately increased by 0.20 eV. Cu\textsubscript{1-x}Li\textsubscript{x}In\textsubscript{0.90}Fe\textsubscript{0.10}S\textsubscript{2}, where x = 0.10, had an estimated band gap slightly higher than that of the x = 0.05 sample. When x = 0.20, a sharp increase of 31%, from the parent compound, was observed in the band gap. This seemed to be anomalous as the x = 0.30 sample only has a band gap of 1.34 eV, a 25% increase over the CuIn\textsubscript{0.90}Fe\textsubscript{0.10}S\textsubscript{2} sample. This anomalous behavior may have been due to a defect structure or the presence of a very minor secondary phase that interfered with the
absorption edge. Again, these changes in the optical absorption edge can be rationalized based on expected changes to the electronic band structure.

**Figure 5.10:** Optical diffuse reflectance spectra converted to absorption for \( \text{Cu}_{1-x}\text{Li}_x\text{In}_{0.90}\text{Fe}_{0.10}\text{S}_2 \), where \( x = 0 - 0.30 \).

There was a greater increase in the band gap (31%) of the Li-Fe-substituted compounds as compared to the Li-substituted materials (17% increase). The larger percent increase in band gap in the Li-Fe-substituted compounds may have been a combination of: 1) the lessening of the antibonding Cu3d – S3p interactions near the VB max and CB min, as in the Li-substituted CuInS2 series which increased the gap between
the VB max and CB min, and 2) the raising of the IB band due to a destabilization of the empty 3d-Fe orbitals as the Fe-S bonds became stronger (Fig.: 5.8). In summary, Li-substitution has proven to increase the band gap of both of the Cu$_{1-x}$Li$_x$InS$_2$ and Cu$_{1-x}$Li$_x$In$_{0.90}$Fe$_{0.10}$S$_2$ series.

5.4 Conclusion

Lithium substitution effectively increased the band gap in both CuInS$_2$ and CuIn$_{0.90}$Fe$_{0.10}$S$_2$, while retaining the chalcopyrite (I-42d) structure. Rietveld refinements of all of the samples (x = 0.05 - 0.30) are indicative of Li residing on the Cu 4a site. As the amount of Li-substitution increased, the cell volume linearly increased as a result of the increase in the bond distance of the Cu/Li-S bond (with the exception of the Cu$_{0.95}$Li$_{0.05}$In$_{0.90}$Fe$_{0.10}$S$_2$ sample, which experienced an increase in the Fe/In-S bond distance). There was a decrease in the In/Fe-S bond length that occurs simultaneously with the increase in the Cu/Li-S bond distance. As the In/Fe-S bond distance decreases, the movement of the sulfur closer to the In/Fe resulted in an x$_s$ closer to 0.25. This indicated that there was less anion displacement from the cubic (zinc blende) parent DLS structure. Heavy doping of CuInS$_2$ using Li or both Li and Fe has resulted in the ability to tune the optical band gap. The band gaps of the Cu$_{1-x}$Li$_x$InS$_2$ series have been shown to increase by 17%, from CuInS$_2$, for the x = 0.30 sample. Even though the addition of iron added an intermediate band above the valence band in CuIn$_{0.90}$Fe$_{0.10}$S$_2$ leading to a decrease in the optical band gap of CuInS$_2$, codoping with lithium in place of copper increased the band gap to within 11% of the unsubstituted CuInS$_2$ band gap. These
increased band gaps of the Cu$_{1-x}$Li$_x$In$_{0.90}$Fe$_{0.10}$S$_2$ series, now fall within the desired range (1.1-1.7 eV)$^{253}$ for promising photovoltaic materials and further evaluation of these materials for solar cell applications is therefore warranted.
5.5 References


XP Highscore Plus, PANalytical B.V., Almelo, the Netherlands.


6 Conclusions

The hypothesis driving this work was that the doping of CuInS$_2$ with iron and/or lithium will elicit property changes in the materials. The motivation behind this work was to develop structure-property and composition-property relationships in diamond-like semiconductors with the use of high-quality, materials characterization tools. The technological impetus was to find a way to make CuInS$_2$ less expensive, by replacing some of the indium, yet still capable of being an excellent photovoltaic compound and to enhance the thermoelectric properties of this solar cell material. Progress made toward each of the specific aims, as outlined in the introduction chapter, is detailed below. Moreover, in light of our progress, future avenues for this work are also proposed at the end of this chapter.

6.1 Major Contributions

The first specific aim of this work was to determine the solubility limit of Fe in place of In in CuInS$_2$, and determine the oxidation states and location of all of the elemental constituents, as well as measuring the band gap of the solid solutions as a function of the dopant concentration. The first step was to ascertain if Fe could be successfully incorporated into the chalcopyrite (I-42d) structure. Analysis of laboratory X-ray data with Rietveld refinement modeling was employed to determine the initial phase purity and structure type of the synthesized material. ICP-OES analysis verified that the actual stoichiometry is in agreement with the intended stoichiometry. With the additional aid of differential thermal analysis and a lattice parameter study, it was
determined that Fe was successfully incorporated into the chalcopyrite (I-42d) structure due to melting point and phase transition temperature changes, and the unit cell volume expansion. It was found that the solubility limit of Fe in CuInS$_2$ is CuIn$_{0.875}$Fe$_{0.125}$S$_2$, and that Fe resides on the In 4b site in the chalcopyrite structure; this could not have been accurately determined without the refinement of models from high-quality neutron and synchrotron powder diffraction data. Laboratory X-ray diffraction did not detect the minute secondary phase present in the CuIn$_{0.85}$Fe$_{0.15}$S$_2$ sample, a phase that was most apparent in the low temperature neutron study, and only weakly present in the synchrotron study.

The location and oxidation state of iron in this series was determined for the first time. It was confirmed that iron is in the 3+ oxidation state. This confirmation of the oxidation state of iron was only possible through Mössbauer spectroscopic analysis. Though XPS reliably confirmed the oxidation states of copper, indium, and sulfur to be 1+, 3+, and 2- respectively, Fe proved to be much more difficult to examine under XPS. XPS is a surface analysis tool, so the surface oxidation on a sample must be sputtered off to investigate the bulk material, and in the case of Fe, the excess surface sputtering reduced the iron, thus making the results unreliable for the determination of the oxidation state of Fe. The Mössbauer spectroscopy revealed the presence of two inequivalent Fe$^{3+}$ ions, indicating that the Fe may be clustering within the crystal lattice. Fe-substitution into CuInS$_2$ introduces an intermediate gap between the valence and conduction band comprised of $d$-Fe orbitals, lowering the optical band gaps of the substituted materials to $\sim$0.70eV. Therefore as predicted, introduction of iron did elicit a change in the property
of the optical absorption edge. Unfortunately the decrease in band gap was too severe, putting the iron-only substituted material out of the ideal range for solar cell applications.

The second specific aim of this investigation was to measure the magnetic and thermoelectric properties of the Fe-substituted materials and complete a more thorough structural study, using neutron diffraction, in order to explore structure-property relationships. Fe-substitution proved to enhance the thermoelectric properties of CuInS$_2$, with CuIn$_{0.875}$Fe$_{0.125}$S$_2$ possessing the highest ZT of the series. The Fe-substitution, specifically for the CuIn$_{0.875}$Fe$_{0.125}$S$_2$ sample, actually has a positive effect on all of the factors that contribute to an increase in ZT. CuIn$_{0.875}$Fe$_{0.125}$S$_2$ experienced an increase in electrical conductivity, an increase in the Seebeck coefficient, and a decrease in thermal conductivity as compared to the undoped CuInS$_2$ parent compound. The presence of iron increased the electrical conductivity, but also provided enough structural complexity to decrease the lattice thermal conductivity. It should be noted that the x = 0.15 sample displayed anomalous behavior for each thermoelectric measurement with the exception of the electrical conductivity measurement, and this was attributed to the impurity phase as revealed by our careful analysis of the diffraction data.

Magnetic susceptibility measurements of CuIn$_{1-x}$Fe$_x$S$_2$ samples, where x ≤ 0.10, indicate that the samples are typical paramagnets. All of these Fe-substituted samples have negative Weiss temperatures which is indicative of a weak antiferromagnetic ordering of the Fe within the compounds. The CuIn$_{0.875}$Fe$_{0.125}$S$_2$ sample also exhibits ferromagnetic ordering at ~95K, and interestingly the CuIn$_{0.85}$Fe$_{0.15}$S$_2$ sample once again displays an anomalous behavior. This sample also exhibits ferromagnetic ordering (~80K), and in addition there is a dominant antiferromagnetic component present (300 -
The ferromagnetic ordering in these materials can be explained by the Fe-clustering that is suggested in the Mössbauer data. The anomalous magnetic and thermoelectric behavior of the $x = 0.15$ sample warranted a high quality neutron and synchrotron powder diffraction study in order to better understand it’s anomalous behavior.

A high-quality structural study of CuIn$_{0.85}$Fe$_{0.15}$S$_2$ provided insight that laboratory X-ray powder diffraction data could not. The low temperature neutron powder diffraction revealed a secondary phase in the $x = 0.15$ sample. This secondary Fe-substituted cubic CuInS$_2$ phase could easily be responsible for the decreased ZT and the presence of an antiferromagnetic component in the sample. Without the advanced structural analysis, the root of the anomalous behavior would never have been discovered. Again as predicted, introduction of iron, not only changed the band gap of the material but also increased its thermoelectric efficiency and induced ferromagnetic ordering at low temperature. With the aim of an arsenal of characterization methods, the ability to understand the structural and chemical changes in the material, in order to propose why this happened, was made possible.

The third specific aim in this study was to determine the solubility limit of Li in place of Cu in both the CuInS$_2$ system and the CuIn$_{0.90}$Fe$_{0.10}$S$_2$ system, as well as measuring the band gap of the solid solution members as a function of the dopant concentrations. Since introduction of Fe in CuInS$_2$ substantially decreased the band gap, additional substitution with lithium was carried out because it was expected to increase the band gap. Li-substitution of both the CuInS$_2$ and CuIn$_{0.90}$Fe$_{0.10}$S$_2$ series proved successful up to $x = 0.30$ under examination of laboratory X-ray powder diffraction, with

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the use of Rietveld refinement. An interesting linear increase in the lattice parameter $a$ and the cell volume was noted. It was found that increasing the Li dopant concentration resulted in a less distorted tetragonal structure which was indicated by a decrease in the anion displacement. As a minimal amount of Fe-substitution was found to lower the band gap of CuInS$_2$, Li-substitution however, increases not only the band gap of CuInS$_2$, but also of CuIn$_{1-x}$Fe$_x$S$_2$ series. The Cu$_{1-x}$Li$_x$InS$_2$ series was found to have a maximum increase in band gap of 17%. The Cu$_{1-x}$Li$_x$In$_{0.90}$Fe$_{0.10}$S$_2$ series realized a maximum increase in band gap of 31%, bringing it fully into the band gap range for possible viable photovoltaic materials.

Through specific aim 3, as in specific aim 1, it was demonstrated that doping in CuInS$_2$ can result in dramatic changes to the properties. This is the first study to explore the solubility of Li in CuInS$_2$ and CuIn$_{0.90}$Fe$_{0.10}$S$_2$, with initial X-ray powder diffraction data and Rietveld refinements suggesting that up to 30% Li substitution is possible. Although the more readily available and less expensive iron was successfully substituted for the costly indium in CuInS$_2$, it came at the price of a band gap below that of the acceptable range for photovoltaic materials. This time success was achieved in bringing the band gap of the substituted material back into the ideal range for photovoltaic energy conversion. More importantly we combined our knowledge of the electronic structure of the parent compounds, with the crystal structure changes observed through Rietveld analysis of X-ray powder diffraction data to correlate the changes in the crystal structure to alterations in the electronic structure and modifications of the property of the optical band gap. These detailed structural studies, that have helped to correlate structure-property relationships, may benefit the future of materials design.
6.2 Comparison to Previous Studies

Although previous work, as explained in chapter 1, has been conducted on Fe-substituted CuInS$_2$ it is through this work that solubility limit, oxidation state and location of iron in CuInS$_2$ has been determined. Previous investigations into the solubility limit and the magnetic behavior of Fe-substituted CuInS$_2$ employed laboratory X-ray powder diffraction, without Rietveld refinements, to determine the phase purity of the materials.$^{254, 255, 256}$ The X-ray powder diffraction data in these studies were not shown in the publications, only referred to, which does not allow for a comparison to the X-ray powder diffraction data in this study. The solubility limit of iron in CuIn$_{1-x}$Fe$_x$S$_2$ in Brun Del Re’s study was determined to be $x = 0.20$, considerably higher than that determined in this work.$^{254}$ The discrepancy could be due to slightly different heating profiles or to the inability of laboratory X-ray powder diffraction to detect minute secondary phases. In this particular case, it is most likely due to the shortcomings of the laboratory XRPD. The first reason to support this idea is that Brun Del Re’s XRPD study employed the analysis of X-ray photographs to determine phase purity.$^{254}$ The instrumentation used in the current study was much more advanced, and as such had a higher detection limit. Secondly, the Mössbauer spectroscopic study of the samples in Brun Del Re’s study revealed the presence of Fe$^{2+}$ in each of the samples, indicating that none of the samples were truly phase pure. Fe$^{2+}$ was never observed in any of the samples in this study. The laboratory XRPD data in the current study, and the subsequent refined models, were also not sufficient enough to determine the true solubility limit of iron in
CuInS$_2$. It was only through the use of high-quality diffraction data, both synchrotron and neutron, that the true solubility limit of CuIn$_{1-x}$Fe$_x$S$_2$ was ascertained.

It was clearly demonstrated that the iron was in the 3+ oxidation state in the materials prepared in this work. On the other hand, Brun Del Re determined the oxidation state of iron to be 2+ and 3+ in CuIn$_{1-x}$Fe$_x$S$_2$, but the oxidation states of the other constituent ions were not determined; however, the likely hood of the Fe$^{2+}$ residing on the Cu site and some of the copper being in the 2+ oxidation state to charge balance it, is discussed but not confirmed.$^{254,255}$ Tsujii reports that the oxidation state of the iron is assumed to be Fe$^{3+}$. $^{256}$ It was in light of Brun Del Re’s Mössbauer spectroscopic study, $^{255}$ revealing the presence of Fe$^{2+}$ that confirmed the necessity of the determination of the oxidation states of all of the constituent ions in the current work. Through the use of XPS and $^{57}$Fe Mössbauer spectroscopy, we can confidently say that Cu, In, Fe, and S are 1+, 3+, 3+, and 2- in our materials.

Although some of the previous researchers assumed Fe to be on the 4b site (indium site) in the chalcopyrite structure, they could not provide any evidence to support this idea. This is mainly because the methods that they employed were insufficient. Because X-ray scattering factors are related to electron density, laboratory X-ray powder diffraction data is not good enough to differentiate between elements near to one another in the periodic table, such as Cu and Fe. In this work X-ray data with the highest resolution was used, from a synchrotron utilizing a short wavelength, which was able to provide a better resolution in differentiating the ions. Additionally, neutron diffraction studies were employed because the neutron scattering factors for the ions under investigation were sufficiently different. Therefore it can be confidently concluded that
the iron, at least in large part, is residing on the 4b site within the structure of these heavily doped materials.

Tsujii’s study was mainly focused on Mn-substituted CuInS\textsubscript{2}, however it did report that CuIn\textsubscript{0.90}Fe\textsubscript{0.10}S\textsubscript{2} exhibits paramagnetic behavior down to 2K.\textsuperscript{256} Brun Del Re completed a much more thorough magnetic study Fe-substituted CuInS\textsubscript{2}.\textsuperscript{255} The Curie-Weiss temperatures (\(\theta\)) for all samples, as in the current work, are reported as negative, suggesting a weak antiferromagnetism. The focus of Brun Del Re’s work is on the samples above \(x = 0.20\), which exhibit spin-glass behavior at lower temperatures and transition to antiferromagnetic at higher temperatures.\textsuperscript{255} In the current work, the \(x = 0.15\) sample exhibits a dominant antiferromagnetic component at high temperature, and a ferromagnetic component at lower temperatures. The spin-glass state in Brun Del Re’s samples may stem from the Fe\textsuperscript{2+} that was not present in the samples being studied in this work. This work clearly showed all iron to be in the 3+ oxidation state, while Brun Del Re’s samples all have a small quantity of Fe\textsuperscript{2+} present (which decreases with decreasing amounts of iron substitution) which can account for the difference in the magnetic measurements for the two works. A high-quality diffraction study can help to determine what secondary phases are present in a sample, which can then lead to a better understanding of complex magnetic properties. The anomalous magnetic and thermoelectric behavior of the CuIn\textsubscript{0.85}Fe\textsubscript{0.15}S\textsubscript{2} sample was explained only through the use of advanced structural analysis, confirming the importance of high quality neutron and synchrotron powder diffraction studies.
6.3 Future Directions

As it was neutron and synchrotron powder diffraction that confirmed the solubility limit of Fe in the CuIn_{1-x}Fe_xS_2 series, it would be interesting to do an extended, high-quality structural study in both the Cu_{1-x}Li_xInS_2 and the Cu_{1-x}Li_xIn_{0.90}Fe_{0.10}S_2 series as well as explore the magnetic properties of both series. The high-quality powder diffraction study could potentially explain the anomalous behavior of some of the samples in chapter 5, particularly the Cu_{1-x}Li_xIn_{0.90}Fe_{0.10}S_2 sample, where x = 0.05.

Fe substitution increased not only the ZT of CuInS_2, but improved every factor that contributes to the ZT of a material; it would be intriguing to apply a similar study like that of this Fe-substituted CuInS_2 study, to a material such as CuInTe_2. CuInTe_2 would be a desirable parent compound as the electrical conductivity is already higher than that of CuInS_2 at 173 Scm^{-1} as compared to 0.03 Scm^{-1}.\textsuperscript{257} The Seebeck coefficient of CuInTe_2 is 283 \mu VK^{-1}, which is much higher than that of CuInS_2 at 145 \mu VK^{-1}.\textsuperscript{257} Not only do the conductivity and Seebeck coefficient make it an attractive starting material, but it also possesses a lower thermal conductivity than CuInS_2 (1.0 Wm^{-1}K^{-1} as compared to 2.14 Wm^{-1}K^{-1}).\textsuperscript{257} However, the study in which CuInTe_2 was shown to have a ZT = 1.18, appeared to have a secondary phase in the X-ray powder patterns,\textsuperscript{257} so it would be imperative to do a high-quality structural study on the parent compound as well as the Fe-substituted compounds to determine what is contributing to this attractive ZT. As Mn-substituted CuInSe_2 realized an increase in ZT of over 2 magnitudes of order, it would also be advisable to undertake a thermoelectric and structural Mn-substituted CuInTe_2 study.\textsuperscript{258} To further aid in the correlation of structure-property relationships, it would be advantageous to study the band gap and the magnetic and thermoelectric
properties of the Mn-Fe-substituted CuInTe$_2$. In order to provide cleaner and more efficient energy in the future, increasing the ZT of these materials as well as tuning the band gap is of upmost importance.

Very little work is being done that investigates the origin of property changes that are elicited by structural changes due to the doping of DLSs. Understanding why thermoelectric and photovoltaic properties have been enhanced by the doping is imperative. More in-depth high-quality structural studies of promising thermoelectric and photovoltaic materials could lead to a better understanding of the structure-property relationships that could potentially be employed as a predictive tool. These tools can then aid in the development of much more efficient, environmentally friendly, and less expensive materials.
6.4 References


